First principles description of response functions in low dimensional systems

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Preliminaries

In the last decades a big effort in both technological and fundamental research has been devoted to what is generically called “nanotechnology”. Even if this is a generic term it can be defined as the understanding and control of matter at the nanometer scale, i.e. the scale of single atoms and small molecules and biology. This has important implications to many fields of research from chemistry to materials science passing by biophysics. In this regime classical physics is not valid anymore and the principles of quantum mechanics have to be applied. Unique phenomena occurring at this scale could enable novel applications [Nalwa 05]. Insight into the nature of microscopic matter has been possible thanks to an increasing and rapid development of optical, electronic and time-resolved spectroscopic techniques that allow more and more precise and detailed measurements and control of the ”nanoworld”. In step with such progress in the field of experimental physics, there has been a big effort by the scientific community to achieve a more detailed theoretical description of the properties of materials at the nanoscale.

Thanks to the recent theoretical developments and the increases in computational power, numerical calculations of real systems have also been made possible. In particular, ab-initio methods are nowadays indispensable for a through understanding of properties and phenomena in low-dimensional structures. Among these, Density Functional Theory (DFT) occupies a dominant place. By replacing the interacting many-electron problem with an effective single-particle problem, DFT allows the density to be computed faster, so it can be used to calculate ground state properties of large systems: remarkable results have been achieved for ground state properties of a huge number of systems ranging from atoms and molecules to solids and surfaces. However, insight into the microscopic nature of matter can only be gained through the interaction of external probes with matter, i.e., through the understanding of excitations (as probed by infrared, Raman, electron and optical spectroscopies for instance) and hence the theoretical prediction of response properties is of fundamental interest. The development of ab-initio techniques that are capable of predicting excited-state quantities, as reliably as, DFT does for the ground state, is a real challenge. In recent years Time Dependent Density Functional Theory (TDDFT) has emerged as a valuable tool for extracting electronic
excited state energies by applying the same philosophy of DFT to time-dependent problems. Its basic variable is the one body density that is obtained from the solution of a fictitious system of non-interacting electrons that evolves in an effective potential $v_s(r, t)$ containing all the many-body effects in its exchange and correlation part. As in the ground state case, it has the big advantage of computational speed with respect to other methods that rely on wave-functions and on the many-body Schrödinger equation. TDDFT can be viewed as an exact alternative reformulation of time-dependent quantum mechanics, nevertheless it has its own drawbacks and cannot be applied with success in all situations. The failures of the theory have to be attributed to the needed approximation of the unknown effective potential $v_s(r, t)$. In any case TDDFT offers a suitable compromise between accuracy and computational efficiency, permitting the description of quite large systems ($\sim 500$ atoms). This feature makes the TDDFT as a suitable tool for the study of sophisticated systems, including phenomena of biological interest. One of the goal of modern biology is the understanding of biological phenomena at the molecular level, which involves the study of the structure of biomolecules and their functions, as well as excited states and interaction between the biomolecules and the electromagnetic field. Biological systems are particularly challenging for ab-initio quantum mechanical methods, nevertheless first principles calculations can be used to attack problems of great current biological interest, that cannot be solved by different approach, and can provide results for comparison with a variety of spectroscopic data.

The application of ab-initio techniques for these classes of complex systems was considered as “utopian” until a few years ago, due to the extremely high degree of complexity. Moreover the TDDFT is perfectly general and can be applied to any time-dependent problem, including the non-perturbative regime, and the description of non linear-phenomena.

The challenge of describing nano and bio structures of potential technological applications imply developments of two sorts: firstly, the proper treatments of many-body effects in simplified, although in principle exact theories (density functional based), secondly the the development of new algorithms and technique, as numerical implementations to speed up the calculations. The present work address both topics, within TDDFT, to describe the response properties of low dimensional structures to external perturbations, in particular the optical properties of low dimensional systems, including biomolecules. The latter would be the focus of a large part of the research done in this thesis. Armed with this theoretical tool we have studied two biological systems of great relevance. First of all we have investigated the
optical properties of DNA bases and base pairs, analyzing in detail the impact of the hydrogen bonding and π stacking in the absorption spectra for both Watson-Crick base pairs and Watson-Crick stacked assemblies. Insight into the excited states of DNA turns to be important not only for understanding crucial phenomena such as radiation-induced DNA damage, but also because of the growing interest in this molecule for various applications in nanotechnology. Secondly, we have successfully employed the method for the description of the linear response of the chromophore of the Green Fluorescent Protein, a molecule whose characteristics of fluorescence and inertness are extensively used in molecular biology as a marker of gene expression. Of course the specific exchange correlation approximations used in TDDFT, like all physical theories, does not work for all systems and situations. For instance, it is known to fail in the description of optical properties of long, conjugated molecular chains. A similar problem is encountered in the calculation of excitations of non-metallic solids when treated with standard functionals. As mentioned before, the origin of this failure has to be attributed to the choice of the exchange and correlation part of the effective potential, and the problem is related to a non local dependence of the xc potential. In order to get insight in this problematic we have studied this class of systems (conjugated linear molecular chains) firstly using Many Body Perturbation Theory (MBPT) and secondly within TDDFT framework, using a new non-local and energy-dependent exchange and correlation potential extracted from the MBPT. Absorption spectra in MBPT have been calculated by means of the Bethe-Salpeter (BS) equation. The BS equation takes into account the electron-hole interaction, which cannot be omitted from a description of neutral excitations (e.g. optical and energy loss spectra), especially for semiconductors and insulators. In the last few years the BS equation has been proved to give remarkably good results for the absorption of a large variety of systems: insulators, semiconductors, atoms, clusters, surfaces and polymers. The absorption spectra calculated by BS equation have been then compared with TDDFT calculations. The obtained results obtained with new functional turn to be of the same precision as the BS, removing the huge error committed by local and gradient-corrected functionals. A lot of work has been done in the last years in order to marry MBPT and TDDFT, this studies have been successful and provide a consistent scheme to include many body effects into TDDFT for solids. The question of validity of this scheme for low dimensional structures, including polymers, nanotubes, biomolecules and nanostructures is still under debate. This thesis shows how all those systems can described on the same footing, providing a consistent theoretical framework to deal with the interaction of
matter with external probe. Of course this is not the final answer as correlations have been introduced at a very simplified level, the next quest would be to add correlation at higher orders that are, of course, relevant for many materials. We hope the present thesis contributes a step forward to achieve this goal. The studied systems are trans-polyacetylene and a molecular hydrogen chain. Trans-polyacetylene is a very well studied conjugated polymer, and is used in a wide range of applications, such as light emitting diodes, photo-diodes and photo-voltaic cells. The molecular hydrogen chain is a model system that can be used to explain different features of real systems by varying the bond length alternation of the chain.

Finally, in the last part of this work, we have studied systems in intense laser fields with electric field strengths that are comparable to the attractive Coulomb field of the nuclei. In this situation the time-dependent field cannot be treated perturbatively; while to solve the time-dependent Schrödinger equation for the evolution of two interacting electrons is barely tractable with present-day computer technology. For such systems TDDFT offers a practical alternative and is able to describe nonlinear phenomena like high-harmonic generation, or multi-photon ionization. In this context we have developed a feasible computational procedure to calculate, within TDDFT, the photo-electron spectrum (PES) of atoms and clusters when excited by short laser pulses. The computational procedure relies on a geometrical approach and provides a description of both energy and angle resolved photo-electron spectra. In order to validate the method we have applied this scheme to a 1D two-electron system and described a energy-resolved and time-resolved two-photon photo-emission experiment on copper surfaces using a 1D model potential.

This dissertation is divided into three parts, and is organized as follows. In the first part, we describe the basic concepts and theories used. In chapter (1) we outline the basic foundation of DFT, while chapter (2) is dedicated to the extension of the theory to time dependent problems (TDDFT) with a particular attention in describing the methods that enable the calculation of excited states. In chapter (3) we give a short introduction to the key concepts of Many Body Perturbation Theory, and the last part of this chapter is focused on the combination of TDDFT and MBPT to describe the new kernel to be used later in chapter (7). The second part of the thesis aims to provide the numerical details and the practical implementations of the theories described in the first part, (this is described in chapter (4)), while in chapter (5) we illustrate a newly developed Coulomb cutoff technique that permits to treat systems that are periodic in less than three dimensions with supercell tech-
niques. This method has been extensively used in the work discussed in chapter (7). The third part of the thesis collects the results of the studied systems: chapter (6) is dedicated to the optical spectroscopy of biological chromophores: the DNA bases and base pairs and the chromophore of the Green Fluorescent Protein. The optical absorption of linear chains and infinite polymers studied with MBPT and TDDFT with the new kernel is discussed in chapter (7). Chapter (8) and (9) are devoted to photo-electron spectroscopy: in chapter (8) we describe our new approach to obtain the photo-electron spectrum within TDDFT, based on geometrical considerations and we apply such method to a model two-electron 1D atom, while in chapter (9) we apply the same scheme to obtain energy-and time-resolved photoemission spectra of image states in Cu(100) and Cu(111) surfaces.
Part I

Basic concepts
The great step made forward by Density Functional Theory (DFT) is to furnish a theoretical basis to a general problem of the Quantum Mechanics: by substituting the many body wave function of an electron system $\Psi(r_1, ..., r_N)$ (defined in a $3N$ dimensional space) with the electron density of the system (a three dimensional function) as basic variable:

$$n(r) = N \int d\mathbf{r}_2 ... d\mathbf{r}_N |\Psi(r, r_2, ..., r_N)|^2$$

(1)

One of the earliest attempt to solve a many body electron problem is due to Hartree [Hartree 28], who approximated the wave function $\Psi$ as a product of single particle wave functions $\psi(r_i)$. Each single particle orbital satisfies a one-electron Schrödinger equation with a local potential arising from the average field of all other electrons. Clearly Hartree’s solution ignores Fermi statistics and produces a fully uncorrelated solution. Slater and Fock [Slater 30, Fock 30] included fermion statistics, writing the wave function $\Psi$ as a single Slater determinant, which leads to the Hartree Fock approximation with a non-local exchange term in the single particle Schrödinger equation. In such approximation electrons of the same spin are correlated, but correlation between electron of different spin is totally neglected. Along this direction, where the many body wave function is the basic variable, there exists a number of methods of increasing complexity. An example of them is the configuration interaction method (CI) where the ground state wave function is a linear combination of a given number of Slater determinant that minimizes the energy. This method leads in principle to the exact many-particle wave-function, but the number of necessary configurations increases drastically with the number of electrons, and the application of such method to large system is prohibitive. A completely different approach was taken by Thomas and Fermi [Thomas 27, Fermi 28], who earlier on proposed a scheme based on the density of the electron system. They assumed that the motions of the electrons are uncorrelated, and that the kinetic energy of a system of density $n$ can be described with a local functional of the density obtained from the kinetic energy of free electrons. Although the Thomas Fermi approximation has only limited success in treating real materials, it is the basis of the density functional formalism. Sharp and Horton [Sharp 53] look to the best local potential that reproduces the non-local Hartree-Fock scheme. This OEP (Optimized Effective Potential) scheme is nowadays widely used in the DFT community to handle orbital-dependent functional, that we will briefly describe later, and it can be considered a firsts step toward the concept of Kohn-Sham orbitals in DFT developed later on in 1965. However, the theoretical foundation that permits this substitu-
tion was established only in the 1964, by Hohenberg and Kohn [Hohenberg 64] who demonstrated that the ground state density of a non degenerate system of interacting electrons determines implicitly all the properties derivable from the Hamiltonian of the system. This is the theoretical basis of the Density Functional Theory (DFT). In a following paper [Kohn 65] Kohn and Sham furnished a practical scheme based on the Hohenberg and Kohn (HK) theorem that permits to solve the many body equation through an auxiliary fictitious non-interacting system that obeys a set of single particle equations, the so-called Kohn-Sham equations (KS).

Currently the DFT and in particular the KS scheme is the most widely used method in electronic structure calculation in the condensed matter physics community. In this chapter we will briefly remind the theoretical foundation of the (DFT) and its time dependent extension: the Time Dependent Density Functional Theory (TDDFT) which are the methods used in most all the works exposed in this thesis. We will not enter here in the mathematical details of the theories, but we will limit to expose the basic principles and explain the main equations that have been extensively used in this thesis, and we refer the reader to the following reviews and books for further details and deeper discussion. For the DFT we refer to Refs [Dreizler 90, Kohn 99, Lundqvist 83, Seminario 96], and for TDDFT to Refs:[Gross 96, Fiolhais 03, Marques 04, Jamorsky 96, van Leeuwen 01, Burke 02]. A recent summary of the TDDFT theory with applications and discussion of all limitations and benefits can be found in[Marques 06]. In the first two chapters we will revise the fundamental theorems that constitutes respectively the basis of the DFT and TDDFT describing also the main approximations used in the practical applications, and in the third section we will describe different schemes that we have employed to calculate excitations energies in TDDFT. With respect the DFT we will follow the derivation of Levy [Levy 79] that it is more general than the original derivation of Hohenberg and Kohn and includes also degenerate ground states. In this chapter we ignore the spin of the electrons, except for considering their fermionic character, and the basic variable will be the spin-less density. For an extension of the theory to the spin-dependent case (useful when treating spin-dependent external-potential or relativistic corrections) we refer to Ref.[Fiolhais 03, von Barth 72]. There exists other extension of the theory as the multicomponent DFT [Kreibich 01] developed to treat both electrons and nuclei quantum mechanically on the same footing and the DFT for superconductors to [Luders 05, Marques 05]. Note that also there exists func-

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1 The Nobel Prize in Chemistry 1998 was awarded to Walter Kohn for his development of the Density Functional Theory.
tional theories based on the current as basic variable (Current DFT). Those are not treated in the present work, therefore we refer the reader to [Vignale 87, Vignale 88] for details. We use atomic units \((e^2 = \hbar = m = 1)\) unless otherwise stated.
1 Basic foundation of DFT

Let us consider a set of systems of N electrons subject to an external potential $\nu(r)$. The Hamiltonian is:

$$H(r_1, r_2, ..., r_N) = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_{r_i}^2 + \nu(r_i)\right) + \frac{1}{2} \sum_{i \neq j}^{N} \nu(r_i, r_j)$$  \hspace{1cm} (1.1)

The Hamiltonian can be cast in the form: $\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}$, where $\hat{T}$ is the kinetic energy operator, $\hat{V}_{ee}$ is the electron-electron interaction and $\hat{V}_{ext} = \sum \nu(i)$ is the external potential. We start by defining the set of N-representable densities $\mathcal{N}_N$. This is the set of the densities $n(r)$ that can be obtained from some antisymmetric wave function of N electrons. Next we define the set of $\nu$-representable densities $\mathcal{N}_\nu$: the set of densities $n(r)$ which are ground-state of any N electron system for some external potential $\nu$. Now we define the Levy-Lieb functional $F$ [Levy 79] as:

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \quad n \in \mathcal{N}_N$$  \hspace{1cm} (1.2)

here the minimum is taken over all the antisymmetric N-electrons wave function that yield the interacting density $n$. The functional $F$ is universal and well defined [Lieb 82]. Let’s denote by $\Psi_{min}[n]$ the wave-function that minimizes the functional for the interacting system for a given density. Now we define a new energy functional with respect to the external potential:

$$E_\nu[n] = F[n] + E_{ext}[n] = F[n] + \int d\mathbf{r} n(\mathbf{r}) \nu(\mathbf{r})$$  \hspace{1cm} (1.3)

where $E_\nu[n]$ is the expectation value of the Hamiltonian evaluated with the state $\Psi_{min}[n]$:

$$E_\nu[n] = \langle \Psi_{min}[n] | \hat{H} | \Psi_{min}[n] \rangle$$  \hspace{1cm} (1.4)

This implies by construction that the energy functional $E_\nu[n]$ is an upper bound for the ground state energy, and present a global minimum at exactly the ground state density:

$$E_\nu[n] \geq E_{GS} \quad \forall n \in \mathcal{N}_\nu$$  \hspace{1cm} (1.5a)

$$E_\nu[n_{GS}] = E_{GS}$$  \hspace{1cm} (1.5b)
Chapter 1. Basic foundation of DFT

To obtain the ground state density we need to minimize $E[n]$ with respect to the density imposing the normalization constrain $\int dr n(r) = N$ with a Lagrange multiplier $\mu$:

$$\frac{\partial F}{\partial n(r)} + \nu(r) = \mu$$

(1.6)

where $\mu$ coincides with the chemical potential. If we rewrite the expression (1.6) for the ground state density:

$$\nu(r) = \mu - \frac{\partial F}{\partial n(r)}[n_{GS}]$$

(1.7)

we learn that the external potential is univocally determined by the ground state density. So if we know the external potential, we know the full Hamiltonian, and this implies in principle the knowledge of all the properties of the system. From those statements we can conclude that the ground state density is enough to extract, in principle, all physical quantities of a fermionic system.

Anyway this does not provide any practical scheme to obtain the ground state density $n_{GS}$. To achieve this purpose Kohn and Sham introduce an auxiliary system of non-interacting electrons having the same density as the interacting one. We denote this system with the letter S. This system is subject to an external potential $S$. The functional $F[n]$ for this fictitious system reduces to:

$$F_S[n] = T_S[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} | \Psi \rangle, \quad n \in \mathcal{N}_N$$

(1.8)

In analogy to Eq. (1.6) for the non-interacting system S we have:

$$\frac{\partial T_S}{\partial n(r)} + \nu_S(r) = \mu$$

(1.9)

By comparing Eq(1.6) and Eq(1.9) we get a formal expression for $\nu_S[n]$:

$$\nu_S[n] = \nu(r) + \frac{\partial F}{\partial n(r)} - \frac{\partial T_S}{\partial n(r)}$$

(1.10)

This implies that the solution of the non-interacting system is the same of the interacting one. In this way we get the interacting density, because we know how to calculate the ground state density of a non-interacting system via its representation in Slater determinant (Kohn-Sham orbitals) and the solutions of the associated single particle equations (Kohn-Sham Equations). In order to make explicit these equations we start by defining the exchange-correlation energy and its functional derivative (the xc potential $v_{xc}$) as:

$$E_{xc}[n] = F[n] - T_S[n] - U[n]$$

(1.11)

$$v_{xc}[n](r) = \frac{\partial E_{xc}}{\partial n(r)}$$

(1.12)
Here \( U[n] \) indicates the classical Hartree electrostatic energy functional:

\[
U[n] = \frac{1}{2} \int d\mathbf{r} n(r) u[n](\mathbf{r}),
\]

and its functional derivative provides the Hartree potential \( v_H(\mathbf{r}) \)

\[
v_H[n](\mathbf{r}) = \frac{\delta U}{\delta n(\mathbf{r})} = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.
\]

Then now we have a close expression for the effective potential \( v_S[n] \) of the non-interacting system:

\[
v_S[n](\mathbf{r}) = \nu(\mathbf{r}) + v_H[n](\mathbf{r}) + v_{xc}[n](\mathbf{r})
\]

This potential is called Kohn-Sham potential \( v_{KS} \). The corresponding Kohn-Sham Hamiltonian will be \( \hat{h}_{KS} = \hat{t} + \hat{v}_{KS}[n] \), where \( \hat{t} \) is the one-particle kinetic operator \([-\nabla^2/2]\). In summary the ground state density of the system can be calculated solving self consistently the following set of Kohn-Sham equations:

\[
\hat{h}_{KS}[n]|\psi_j\rangle = \epsilon_j |\psi_j\rangle \tag{1.16a}
\]

\[
\hat{h}_{KS}[n] = -\frac{1}{2} \nabla^2 + \nu(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r}) \tag{1.16b}
\]

\[
n(\mathbf{r}) = \sum_j \theta(\mu - \epsilon_j) \psi_j^\ast(\mathbf{r}) \psi_j(\mathbf{r}) \tag{1.16c}
\]

\[
\int d\mathbf{r} n(\mathbf{r}) = N \tag{1.16d}
\]

where \( \psi_j \), are the one particle wave function that are solution of the non-interacting problem Eq. (1.16a). The Fermi level \( \mu \) of Eq. (1.9) is determined by the fulfillment of Eq. (1.16d). Thus, the ground state total energy \( E_{GS} \) of the interacting system is given by:

\[
E_{GS} = \sum_j \theta(\mu - \epsilon_j) \epsilon_j - U[n] - \int d\mathbf{r} n(\mathbf{r}) v_{xc}[n](\mathbf{r}) + E_{xc}[n] \tag{1.17}
\]

In principle the solution of the Kohn-Sham equation with the \textit{exact} exchange-correlation potential, would give single particle eigenstates which density equals the exact density of the interacting system. Clearly the \textit{exact} xc-potential, which includes all non-trivial many body effects, it is unknown and has to be approximated. The \( E_{xc}[n] \) term, even if it is a small part of the total energy for typical chemical system, it is of the order of magnitude of the atomization energy, the relevant magnitude in Chemistry, so good approximations are required. We will show later how Many-body perturbation theory can be used to improve available xc-functionals for electronic properties.
1.1 Approximation to the Exchange and Correlation Functionals

The research on the optimal exchange-correlation potential has been a flourishing field of research in the last decades, and very good xc-functionals are now available. One of the most widely used and simplest approximation, is the Local Density Approximation (LDA). In this thesis this has been the most used approximation for our ground state calculation. However when needed we compare with more precise schemes as GGA’s. Introducing the exchange-correlation energy density $\epsilon_{xc}(\{n\}; \mathbf{r})$, we can write the xc Energy as:

$$ E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}(\{n\}; \mathbf{r}). $$

the LDA assumes that the system *locally* appears as an homogeneous electron gas of the same density as the inhomogeneous system:

$$ E_{xc}^{LDA}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}^{HEG}(\{n\})(\mathbf{r}) $$

$\epsilon_{xc}^{HEG}(\{n\}; \mathbf{r})$ is split in its bare exchange part and correlation part. While the exchange part is an analytic function of $n$ [Fetter 81].

$$ \epsilon_{xc}^{HEG}(n(\mathbf{r})) = -\frac{3}{4} \left[ \frac{3n}{\pi} \right]^{1/3} $$

the correlation part can be approximated using Many Body perturbation theory [Hedin 71], or obtained from Quantum Montecarlo methods [Ceperley 80]. The results from Quantum Montecarlo calculation has been parametrized by, e.g. Perdew and Zunger [Perdew 81] and also allow the treatment of spin polarized system (local spin density approximation LSD). In this thesis, however, we have considered only the case if spin compensated systems. The correlation part is given by:

$$ \epsilon_{c}^{HEG}(n(\mathbf{r})) = \gamma / (1 + \beta_1 \sqrt{r_s} + \beta_2 r_s), \quad r_s \geq 1 $$

where $r_s$ is defined by:

$$ \frac{1}{n(\mathbf{r})} = \frac{4}{3} \pi r_s^3 $$

and $\gamma = -0.14230$, $\beta_1 = 1.05290$, $\beta_2 = 0.3334$. The LDA approximation should be a good approximation for systems with slow varying density. Anyway LDA has

---

1 For example see: J. P.Perdew and S. Kurth in Chap.1 of [Fiolhais 03]
been applied successfully for a big amount of systems, and its success rely to error cancellations [Dreizler 90, Jones 89], and from the fact that important sum rules are exactly satisfied in LDA. Nevertheless we have to mention several shortcomings of the LDA among that:

- The LDA does not work for system where the density has strong spatial variations or for weakly interacting system as Van der Waals bonded molecules. It usually overestimates correlation and underestimates exchange.

- The exchange part of the functional does not cancel the self-energy part of the Hartree term with the consequence of a wrong asymptotic behavior of the xc potential for finite systems. Such shortcomings leads to wrong estimation of ionization potentials of atoms and molecules, Rydberg states are not present in LDA and negative ions usually does not bind.

Another class of functionals that we also used in this thesis is the so-called Generalized Gradient Approximated (GGA) functionals [Becke 88, Lee 88, Perdew 96]. For these functionals the exchange-correlation energy is written as:

$$E_{xc}^{GGA}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}^{GGA}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$ (1.23)

$\epsilon_{xc}^{GGA}$ is some analytic function of the density and the gradient of the density with some free parameters, that are either fitted to experiments or obtained from sum rules. The GGA functionals solve some of the problems present in LDA, in general atomic and molecular total energies are improved, and are extensively used in quantum chemistry calculations. Recently another family of functionals has been introduced that generalize the GGA approximation, called Meta-GGA functionals [Perdew 99], where $\epsilon_{xc}^{MCGA}$ is now a functional not only of the density and its gradient, but also of the kinetic energy density $^2$. Such extra-dependence permits to have more flexibility and more precise approximations to the exact xc functional have been obtained. Anyway neither the GGA nor the MGGA approximations solve the self-interaction problem. We finish this section mentioning another class of xc-potential that we have also used in this thesis, the so-called Optimize Effective Potential (OEP)$^3$. This family of potential is formed by functionals that have an explicitly dependence on the Kohn-Sham orbitals thus are only implicitly functional.

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$^2$ Due to the dependence on the kinetic energy density, the MGGA, are orbital functionals.

$^3$ For a review on this generation of functional see i.e.: E.Engel in Chap.2 of [Fiolhais 03]
Chapter 1. Basic foundation of DFT

of the density. Thus, the OEP scheme looks for the local potential that minimize the energy functional with respect to the density.

\[ E_{xc}^{OEP} = E_{xc}^{OEP}[\psi_1(\mathbf{r}) \ldots \psi_N(\mathbf{r})] \]  

(1.24)

The xc potential is then calculated via Eq. (1.12) using the chain rules for functional derivatives:

\[ v_{xc}^{OEP}[n](\mathbf{r}) = \frac{\delta E_{xc}^{OEP}}{\delta n(\mathbf{r})} = \sum_{i=1}^{N} \int d\mathbf{r}' d\mathbf{r}'' \left[ \frac{\delta E_{xc}^{OEP}}{\delta \psi_i(\mathbf{r}')} \frac{\delta \psi_i(\mathbf{r}')}{\delta v_{ks}(\mathbf{r}'')} + c.c \right] \frac{\delta v_{ks}(\mathbf{r}'')}{\delta n(\mathbf{r})} \]  

(1.25)

Here the term \( \frac{\delta E_{xc}^{OEP}}{\delta \psi_i(\mathbf{r})} \) is obtained from the expression of \( E_{xc}^{OEP}[\psi_1(\mathbf{r}) \ldots \psi_N(\mathbf{r})] \), the second derivatives \( \frac{\delta \psi_i(\mathbf{r})}{\delta v_{ks}(\mathbf{r}'')} \) can be calculated using first order perturbation theory and finally \( \frac{\delta v_{ks}(\mathbf{r}'')}{\delta n(\mathbf{r})} \) is the inverse of the Kohn-Sham response function as we will see in section (2.2). Equation (1.25) can be recast in an integral equation for \( v_{xc}^{OEP} \). An example of these orbitals functional is the exact exchange (EXX) potential that is derived applying the OEP-scheme to the exact expression for the exchange energy:

\[ E_{EX}^{EXX} = -\frac{1}{2} \sum_{\sigma} \sum_{i,j=1}^{N} \int d\mathbf{r} d\mathbf{r}' \frac{\psi_{i\sigma}(\mathbf{r}) \psi_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \]  

(1.26)

Note that the \( E_{EX}^{EXX} \) functional cancels the self-interaction part of the Hartree energy and the exact exchange potential has the correct asymptotic behavior. Anyway, the solution of the equations to get such xc potentials turns to be numerically demanding, and approximations has been proposed to simplify the problem. In the present work, (see section (7.4)), we have considered KS wave functions and energies, by solving the OEP equation for the \( E_{EX}^{EXX} \) within the Krieg-Li-Iafrate[Krieger 92] (KLI) approximation:

\[ v_{x}^{KLI} = \frac{1}{2n(\mathbf{r})} \sum_{j} \left\{ \left[ \psi_{j}(\mathbf{r}) \frac{\delta E_{EX}^{EXX}}{\delta \psi_{j}(\mathbf{r})} \right] + |\psi_{j}(\mathbf{r})|^2 \Delta v_{j}^{KLI} \right\} \]  

(1.27a)

\[ \Delta v_{j}^{KLI} = \int d\mathbf{r} \left\{ \theta(\epsilon_j - \mu)|\psi_{j}(\mathbf{r})|^2 v_{x}^{KLI}(\mathbf{r}) - \psi_{j}^{*}(\mathbf{r}) \frac{\delta E_{EX}^{EXX}}{\delta \psi_{j}^{*}(\mathbf{r})} \right\} + c.c \]  

(1.27b)

The \( v_{x}^{KLI} \) then can be solved both by transforming the integral equations (1.27) in a set of linear equations [Krieger 90] or one can iterate Eq. (1.27) until self-consistency. It turn out that for most of the system studied the KLI approximation is very close to the exact OEP solution [Fiohlais 03].
1.2 Some problems and pathologies of present xc functionals

1.2.1 The Band Gap problem

Before concluding this short description of the main feature of the DFT it is important to emphasize that the KS eigenvalues obtained from Eq. 1.16a does not have a physical meaning, except the highest occupied eigenvalues $\epsilon^{(N)}_{N}$ which equals the ionization potential of the system [Levy 84, Almbladh 85]. Even if the relative values of the occupied KS eigenvalues are in rather good agreement with the experiment for semiconductor and insulators, the band gaps are underestimated by about 50% up to 100%[Hybertsen 85, Hybertsen 86, Godby 86, Godby 87a, Godby 87b, Godby 88].

The exact band gap for an $N$ electron system is defined by:

$$E_{\text{gap}} = E^{(N+1)} - E^{(N)} - (E^{(N)} - E^{(N-1)}) = \epsilon^{(N+1)}_{N+1} - \epsilon^{(N)}_{N}$$  \hspace{1cm} (1.28)

i.e the difference between the electron affinity and the ionization potential. For the fictitious Kohn-Sham system we have:

$$E_{\text{gap}}^{KS} = \epsilon^{(N)}_{N+1} - \epsilon^{(N)}_{N}$$  \hspace{1cm} (1.29)

From Eq. (1.28) and Eq. (1.29) we have:

$$E_{\text{gap}} = E_{\text{gap}}^{KS} + \Delta_{xc}$$  \hspace{1cm} (1.30)

We may see that the quantity $\Delta_{xc}$ is the difference between the energies of the $(N+1)$-th orbitals of the KS systems that correspond to the neutral and ionized electron system. The addition of an extra electron only induces an infinitesimal change of the density, so a discontinuity of order one have to be assigned to a discontinuity in the xc-potential, which is not necessarily analytic in $N$, in contrast to the Hartree potential:

$$\Delta_{xc} = V_{xc}^{(N+1)}(r) - V_{xc}^{(N)}(r)$$  \hspace{1cm} (1.31)

There is evidence [Godby 88] that the xc discontinuity $\Delta_{xc}$, rather than the local density approximation, is the main cause of the big discrepancy between the experimental values and the one found in DFT-LDA for typical semiconductors and insulators. Thus we can say that the band gap problem is not an intrinsic feature.

\footnote{Here with $\epsilon^{(N)}_{N}$ we indicate the $N$-th eigenvalue of an $(N)$-electron system.}
of the DFT nor of the LDA but of the Kohn-Sham scheme. In section (3.3) we will see how realistic energies of adding/removing electron to/from the system can be calculated within the quasiparticle formalism.

1.2.2 The xc Electric Field

Another important pathology of the exchange correlation potential $v_{xc}(r)$ is the so-called exchange-correlation electric field [Godby 90, Godby 94, Gonze 95, Gonze 97a, Gonze 97b, Ghosez 97]. If we consider an insulating solid subjected to an external uniform electric field, the electrons in response of the electric field will generates in each unit cell en electric dipole moment. The effect of the response of the electron will be a macroscopic polarization, and consequently a depolarizing electric field that counteracts the external potential. If now we switch to the Kohn-Sham system, Gonze et al. [Gonze 95] showed that the applied perturbing potential it is not a unique functional of the periodic density, but it depends also on the change in the macroscopic polarization, that is, on the electronic density at the surface of the crystal. Moreover, the dependence of the exchange-correlation energy on polarization induces an exchange-correlation electric field. This situation is drawn in Fig.(1.1). In the upper part is sketched the density charge and the KS potential of an unpolarized insulator. When the electric field is applied (central and bottom part of the figure), the insulator is polarized and we see in the figure that two different Kohn-Sham potential, one with zero net long range behavior (bottom part) and one with a part that vary linearly in space (central panel), that reproduce the same bulk density. The two potentials correspond to two different values of the macroscopic polarizabilities. In particular it exists a family of potentials with different net long range part, that gives the same bulk density and produce a different macroscopic polarization. In order to reproduce the correct macroscopic polarization the exchange correlation potentials must have a particular non zero long range part. This part of the exchange correlation potential it is the exchange-correlation electric field. Therefore it is clear that the $v_{xc}(r)$ cannot be a functional of the density alone in the unit cell, the electronic density is the same from a unit cell to the other, while the potential rise linearly. Such feature of the exact exchange correlation potential it is called spatial ultra non locality. It can be easily understood that the exchange correlation electric field is totally absent in both LDA and GGA approximation, but it is present in more non-local functionals like the EXX [van Gisbergen 99, Gritsenko 01]. For finite systems this ultra-nonlocality appears as an internal xc-field. This field is
1.2 Some problems and pathologies of present \( xc \) functionals

Figure 1.1: Schematic illustration of the bulk density and Kohn Sham potential for an insulator. Top: the unpolarized case. Center: the same insulator subjected to an uniform electric field: the exchange and correlation potential develop a term linear in space: the \( xc \) electric field. Bottom: the same insulator with a KS potential without a net long-range field. The density is the same as the case illustrated in the center, but the two situation have different macroscopic polarization. Figure adapted from R. Godby and P. García Gonzalez in Chap.5 of [Fiolhais 03]

extremely important to describe the optical properties of chains of atoms, polymers etc. (see section (7)).
2 Time-dependent DFT (TDDFT)

2.1 Basic theorems

Time Dependent Density Functional Theory (TDDFT) is the extension of the DFT to time dependent phenomena\(^1\). It permits calculation of excited states, but its potentiality goes further because essentially it is at all effects an exact reformulation of the time dependent Schrödinger equation and can be applied to describe in general time-dependent phenomena beyond equilibrium. TDDFT is based on the Runge-Gross theorem [Runge 84] that states:

\[ \text{given a system of electrons prepared in a given initial state } |\Phi(t_0)\rangle, \text{ there is} \]

a biunivocal correspondence between the external time-dependent potential \( v_{\text{ext}}(r, t) \) and the time-dependent electron density \( n(r, t) \).

This is a generalization to time-dependent potentials and density, of the ordinary DFT one-to-one correspondence:

\[ n(r, t) \leftrightarrow v(r, t), \quad (2.1) \]

Note that in this case:

- Two potentials are considered equivalent if they differ by any purely time-dependent function.
- There is a dependence on the initial quantum state of the system.
- Contrary to intuition, the \( v \)-representability problem (the problem of the existence of a potential that produces a given density) is milder in the time-dependent case than in the stationary case, and has been solved by van Leeuwen [van Leeuwen 99] under a very broad assumptions for the initial state of the system: moreover it gave an implicit form of constructing the \( v_{xc}(r, t) \).

\(^1\) For a general overview see [Marques 06]
By virtue of the Runge Gross theorem, as in the static case, a fictitious Kohn-Sham scheme can be introduced by considering a system of non-interacting electrons subject to an external potential \( v_{KS}(r, t) \) that reproduces the exact time dependent density \( n(r, t) \) of the interacting system. The time-dependent density is obtained propagating a set of a Schrödinger like equations, the time-dependent Kohn-Sham equations (TDKS) where all the many-body effects are included through a time-dependent exchange-correlation potential. This potential is unknown, and has to be approximated in any practical application of the theory. The TDKS equations looks like:

\[
 i \frac{\partial}{\partial t} \psi_i(r, t) = \left[- \frac{\nabla^2}{2} + v_{KS}[n](r, t)\right] \psi_i(r, t) \tag{2.2}
\]

The density of the interacting system can be obtained from the time-dependent Kohn-Sham orbitals:

\[
 n(r, t) = \sum_{\text{occ}} |\psi_i(r, t)|^2. \tag{2.3}
\]

The Kohn-Sham potential is conventionally separated in the following way:

\[
 v_{KS}(r, t) = v_{\text{ext}}(r, t) + v_{H}(r, t) + v_{xc}(r, t) \tag{2.4}
\]

The first term is the external potential, the second term (Hartree potential) accounts for the classical electrostatic interactions between electrons:

\[
 v_{H}(r, t) = \int d\mathbf{r}' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \tag{2.5}
\]

The last term, the xc potential, includes all the non-trivial many body effects. In the static case (DFT) the xc potentials is derived as a functional derivatives of the xc energy Eq. (1.12), and it is not straightforward to extend such derivation in the time-dependent case due to a problem of causality [Gross 95, Gross 96]. This problem has been solved by Van Leeuwen [van Leeuwen 98], introducing a new action functional \( \tilde{A} \) in the Keldish formalism. The time-dependent xc potential can be then written as the functional derivative of the xc part of this action \( \tilde{A} \).

\[
 v_{xc}[n](r, t) = \frac{\partial \tilde{A}_{xc}}{\partial n(\mathbf{r}, \tau)} \bigg|_{n(r, t)} \tag{2.6}
\]

where \( \tau \) stands for the Keldish pseudo-time.

In any case the exact expression of \( v_{xc} \) as a functional of the density is unknown and the quality of any calculation will depend on the quality of the approximation of this term. It is important to note that this is the only fundamental approximation in
2.2 Excitation energies in TDDFT

TDDFT. Before concluding this section we define the so-called exchange-correlation kernel \( f_{xc} \):

\[
f_{xc}(r, r', \omega) = \left. \frac{\delta v_{xc}[n(r, \omega)]}{\delta n(r', \omega)} \right|_{\delta v_{ext}=0}
\]

(2.7)

whose importance will be clear in the next session. In contrast with the ground state DFT where very good \( xc \) potential exists, approximations to \( v_{xc}(r, t) \) are still in their infancy. Anyway the simplest approximations to the \( xc \) functional in TDDFT is the adiabatic approximation, which use existing \( xc \) functionals for the ground state in the time-dependent case. It consists in evaluating the ground state functional at each time with the density \( n(r, t) \):

\[
v_{xc}^{adiabatic}(r, t) = v_{xc}^{\text{LDA}}(r)\big|_{n=n(t)}
\]

(2.8)

where we have indicate with \( v_{xc}^{\text{LDA}} \) an approximation to the ground state density \( xc \) functional. Such time-dependent functional is of course local in time, and this turns to be a quite drastic approximation, and we expect to work only in the case where the temporal dependence is small. In the case of the LDA, we obtain the so-called Adiabatic Local Density Approximations (ALDA), that is one of the most widely used functional that reads:

\[
v_{xc}^{ALDA}(r, t) = v_{xc}^{\text{HEG}}(n)\big|_{n=n(r, t)}
\]

(2.9)

Of course the ALDA retains all the problems present in the LDA as for example the wrong asymptotic behavior. In the ALDA, the \( f_{xc} \) kernel is a contact function both in time and space:

\[
f_{xc}^{ALDA}(r, t, r', t') = \delta(t - t')\delta(r - r')\frac{dv_{xc}^{\text{LDA}}(n)}{dn}\big|_{n=n(r, t)}
\]

(2.10)

Despite these problems, ALDA yields remarkably good results for finite systems and has been used in some works discussed in this thesis. Of course there exist case where such approximation dramatically fails and it is necessary to resort to much more complicate functionals as in chapter (7). In particular the ALDA misses the important \( 1/q^2 \) divergence that controls the optical absorption of extended systems with gap.

2.2 Excitation energies in TDDFT

In order to determine observable properties such as dynamical polarizability, absorption spectra and excitations energies, the fundamental quantity is the linear i
response of the electronic system, i.e. the response of the system when perturbed by a weak time-dependent external electric potential $\delta w(r, t)$. This perturbation will induces a time-dependent perturbation of the density $\delta n(r, t)$, that can be related to the perturbing potential by:

$$\delta n(r, \omega) = \int dr' \chi(r, r', \omega) \delta w(r', \omega). \quad (2.11)$$

where the function $\chi(r, r', \omega)$ is the so called density-density response function. The linear response of a molecule can be described via the dynamical polarizability tensor i.e.:

$$\delta \mu_i(\omega) = \sum_j \alpha_{ij}(\omega) E_j(\omega) \quad (2.12)$$

where $\delta \mu_i(\omega) = \int dr x_i \delta n(r, \omega)$ is the induced dipole in the i direction and $E_j(\omega)$ is the external applied field. Assuming a dipolar perturbation, i.e. $\delta v(r, \omega) = -E(\omega) \cdot r$ the polarizability tensor can be related to the response function by:

$$\alpha_{ij}(\omega) = -\int \int dr dr' x_i(r, r', \omega) x_j \quad (2.13)$$

The imaginary part of the polarizability is then related to the photo-absorption cross section $\sigma(\omega)$, the relevant magnitude measured in experiment, by:

$$\sigma(\omega) = \frac{4\pi \omega}{c} \frac{1}{3} \Im[\text{Tr}\alpha(\omega)]. \quad (2.14)$$

Now we illustrate how TDDFT allows to calculate the excited state energies of a many body system, starting from the knowledge of the ground state of the system, obtained for instance from a self-consistent DFT approach. The induced density of Eq. (2.11) must be the same in the interacting and in the Kohn-Sham system, so we can write the induced density $\delta n(r, \omega)$ as:

$$\delta n(r, \omega) = \int dr' \chi_{KS}(r, r', \omega) \delta v_{KS}(r', \omega). \quad (2.15)$$

where $\delta v_{KS}$ includes the external potential and the induced Hartree potential and the exchange and correlation potential. Such potential expressed in terms of the xc kernel $f_{xc}$ (the functional derivative of the xc potential Eq. (2.7)) reads:

$$\delta v_{KS}(r, \omega) = \delta w(r, \omega) + \int dr' \frac{\delta n(r', \omega)}{|r - r'|} + \int dr' f_{xc}(r, r', \omega) \delta n(r'). \quad (2.16)$$

For a time independent Hamiltonian the polarizability depend only on the time-differences and a Fourier Transform in energy space can be easily performed.
The Kohn-Sham response function \( \chi_{KS}(r, r', \omega) \) is the response function of a fictitious non-interacting system, thus applying first order perturbation theory to KS equations (1.16a), it can be expressed in terms of the ground state Kohn-Sham eigenvalues \( \epsilon_i \) and eigenfunctions \( \psi_i \):

\[
\chi_{KS}(r, r', \omega) = \sum_{ij} (f_i - f_j) \frac{\psi_i(r) \psi_j^*(r') \psi_j(r') \psi_i^*(r)}{\omega - \omega_{ij} + i\eta} \tag{2.17}
\]

where \( \omega_{ij} = (\epsilon_i - \epsilon_j) \) and \( f_i \) is the occupation number of the Kohn-Sham orbitals. Combining Eqs (2.11) and (2.15) we arrive at the Dyson equation for the interacting response function:

\[
\chi(r, r', \omega) = \chi_{KS}(r, r', \omega) + \int d\mathbf{r}_1 \mathbf{r}_2 \chi_{KS}(\mathbf{r}, \mathbf{r}_1, \omega) \left[ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega) \right] \chi(\mathbf{r}_2, \mathbf{r}', \omega), \tag{2.18}
\]

The solution of Eq. (2.18) provides in line of principle the exact full interacting density response function: the poles of \( \chi \) are the excitation energies of the system as we will see below, so this equation allows to determine the exact excitation energies of the system once the Kohn-Sham \( \chi_{KS} \) and the xc kernel \( f_{xc} \) are known. Here we note that with the approximation \( f_{xc} = 0 \) we obtain the so called random phase approximation (RPA) of the response function. In any case, a full solution of Eq. (2.18) turns to be a difficult task from numerical point of view. Besides the computational effort requires to solve the integral equation, it requires the non interacting response function Eq. (2.17) that involve summations of both occupied and unoccupied states, and such summations are sometimes slowly convergent, and inclusion of a big amount of unoccupied states is required. In the following subsections we will describe the main ideas of the two different approaches to calculate excitation energies that have been extensively used in the works reported in this thesis: first we will present the matrix eigenvalue method that resort to the Linear Response Theory, next we describe a method based in the full solution of the time dependent Kohn-Sham equations Eq. (2.2).

### 2.2.1 Matrix eigenvalue method

A way to circumvent the difficulty of solving Eq. (2.18) for systems with discrete spectrum such as molecules, starts by writing the Lehmann representation of the interacting density response function:

\[
\chi(r, r', \omega) = \lim_{\eta \to 0^+} \sum_m \left[ \frac{\langle 0|\hat{n}(r)|m\rangle \langle m|\hat{n}(r')|0\rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0|\hat{n}(r)|m\rangle \langle m|\hat{n}(r')|0\rangle}{\omega + (E_m - E_0) + i\eta} \right] \tag{2.19}
\]
where $|m\rangle$ and $E_m$ are the many body eigenstates and energies of the interacting system and with $|0\rangle$ we have indicated the ground state. We see from Eq. (2.19) that the density response function presents poles at the excitation energies of the system $\omega = \Omega_m = E_m - E_0$. This implies from Eq. (2.11) that also the induced density has poles at the excitation energies $\Omega_m$ because the external potential does not have any special pole structure in function of $\omega$. Looking at Eq. (2.17) we see that the non-interacting Kohn-Sham response function has poles at the Kohn-Sham eigenvalues differences $\omega_{ij} = \epsilon_i - \epsilon_j$. From this consideration, rearranging Eq. (2.15) and (2.16), one can derive the following eigenvalue equation [Petersilka 96]:

$$\int dr' \Xi(r, r', \omega) \xi(r', \omega) = \lambda(\omega) \xi(r, \omega)$$

where the kernel $\Xi$ is defined as:

$$\Xi(r, r', \omega) = \delta(r - r') - \int ds \chi_{KS}(r, s, \omega) \left[ \frac{1}{|s - r'|} + f_{xc}(s, r', \omega) \right].$$

Note that $\lambda(\omega) \to 1$ when $\omega$ coincide with the excitation energy $\Omega$. Next, it is possible to transform this eigenvalues equation, to another one whose eigenvalues are true excitation energies [Jamorsky 96]. Expanding $\xi(r, \omega)$ in a basis set made of products of occupied and unoccupied states we find the following matrix equation:

$$\Theta(\Omega) \bar{F}_I = \Omega^2 \bar{F}_I$$

where the operator $\Theta(\Omega)$ is given by:

$$\Theta_{ij\sigma,kl\tau}(\Omega) = \delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l} \omega_{kl}^2 + 2 \sqrt{(f_{1\sigma} - f_{1\sigma}) \omega_{ij} K_{ij\sigma,kl\tau}(\Omega) \sqrt{(f_{1\tau} - f_{1\tau}) \omega_{kl}}}$$

where the indexes $(i, j)$ and $(k, l)$ run over single particle orbitals, $(\sigma, \tau)$ are spin indexes, and $\omega_{ij\sigma} = \epsilon_{ij\sigma}$. Note that here we have introduced the spin variables in order to treat also triplet excitations as will be discussed in chapter (7). The Kernel $K_{ij\sigma,kl\tau}(\Omega)$ is given by:

$$K_{ij\sigma,kl\tau}(\Omega) = \int d^3r \int d^3r' \psi_{i\sigma}^*(r) \psi_{j\tau}(r') \left[ \frac{1}{|r - r'|} + f_{xc,\sigma\tau}(r, r', \Omega) \right] \psi_{k\tau}(r') \psi_{l\sigma}^*(r')$$

Eq. (2.22) gives the exact position of the excitation energies $\Omega$, and the corresponding oscillator strengths are obtained from the eigenvectors of the operator $\Theta$. It is important to stress that the quality of the excitation energies will depend from the truncation of the expansion, the used approximation for the unknown kernel $f_{xc}$ and
2.2 Excitation energies in TDDFT

for the exchange-correlation potential used for the calculation of the ground state Kohn-Sham orbitals. The solution of Eq. (2.22) turns out to be computationally really cumbersome, and it is possible to reduce such complexity paying the price of loosing accuracy [Petersilka 96]. Assuming that the true excitation does not differ to much from a single particle excitation it is possible to perform a Laurent expansion of $\chi_{KS}$ around one particle energy difference between the Kohn-Sham eigenvalues $\omega_{j_0k_0} = \epsilon_{k_0} - \epsilon_{j_0}$:

$$\chi_{KS}(r, r', \omega) = \lim_{\eta \to 0} \frac{\psi_{j_0}(r)\psi_{j_0}^*(r')\psi_{k_0}(r')\psi_{k_0}^*(r)}{\omega - \omega_{j_0k_0} + i\eta} + \text{higher orders.} \quad (2.25)$$

Neglecting the higher orders terms such approximation leads to the so-called Single Pole Approximation (SPA):

$$\Omega \approx \omega_{j_0k_0} + K(\omega_{j_0k_0}) \quad (2.26)$$

where the term $K$ for the singlet excitation is given by:

$$K(\omega_{j_0k_0}) = 2\Re \int dr \int dr' \psi_{j_0}(r)\psi_{j_0}^*(r')\psi_{k_0}(r')\psi_{k_0}^*(r)\frac{1}{|r - r'|} + f_{xc}(r, r', \omega_{j_0k_0})$$ \quad (2.27)

Here the term $K$ can be viewed as a correction factor to the Kohn-Sham excitation energies. Such approximation (SPA) although it is not precise as the full solution of Eq. (2.22) provides a fast way to calculate excitation energies and turns to be a very good approximation for many system as discussed in Refs. [Gonze 99, Appel 03]. From these considerations we can conclude that the crucial approximation for the calculation of excited states in TDDFT is the choice of the static xc potential used to calculate the Kohn-Sham eigenfunctions and eigenvalues. Moreover an important feature of the calculation of excited states using the matrix eigenvalue method is that it is possible to give a qualitative assignment of the character of the excited state $\Psi_I$. Such assignment it is not possible solving directly the time dependent Kohn-Sham equations, because as we will see in the next section, such method is based on the time dependent density and no information on the wave functions is available. If we first expand the excited state $\Psi_I$ in single excited configurations as:

$$\Psi_I = \sum_{i,j,\sigma} \frac{f_{i\sigma} - f_{j\sigma} > 0}{\epsilon_{ij\sigma}^F} \hat{a}_{ji\sigma}^\dagger \hat{a}_{j\sigma} \Phi + \cdots \quad (2.28)$$

$^3$ Here we are considering a spin-unpolarized system. The extension to spin polarized systems is straightforward, even if more complicated and the mixing of spin channel comes from the exchange correlation kernel $f_{xc,\sigma\tau}$.
assuming that the ground state wave function $\Psi_0$ is a single determinant of Kohn Sham orbitals and that matrix elements:

$$x_{ij\sigma} = \int \psi_{i\sigma}(\mathbf{r}) \hat{x} \psi_{j\sigma}(\mathbf{r}),$$  \hspace{1cm} (2.29)

are linearly independent, it is possible to calculate the coefficients of the expansion in Eq. (2.28) by:

$$c_{ij\sigma}^I = \sqrt{\frac{\epsilon_{j\sigma} - \epsilon_{i\sigma}}{\Omega_I}} \Gamma_{ij\sigma}^I.$$  \hspace{1cm} (2.30)

This expression, gives a weight of each single particle excitations that contribute to a given excited state $\Psi_I$, and turn to be useful in order to assign a character to the excitations, even if qualitative.

### 2.2.2 Full solution in real time of the TDDFT Kohn-Sham equations

In order to calculate the linear and non-linear response functions of finite systems, a very efficient method consists in the direct solution of the time dependent Kohn-Sham equations Eq. (2.2). Such method was originally proposed to solve time dependent Hartree Fock equations for studying nuclear reactions by Flocard and coworkers [Flocard 78] and later has been used with success for TDDFT calculations of photo-absorption for clusters [Yabana 96, Yabana 97, Yabana 99a, Yabana 99b, Marques 01, Castro 02, Martinez 04] and biomolecules [Marques 03b, Varsano 05, Tsolakidis 05]. Moreover this methods has been applied to study laser induced fragmentation problems and high harmonic generation [Castro 04b]. The starting point for the solution of the time dependent problem is the initial state of the electronic system: the Kohn-Sham ground state. Then we apply the external time-dependent field and propagate the time-dependent KS equations following an unitary scheme [Marques 03a, Castro 04c]. Then, in the particular case one is interested in obtaining the linear optical absorption the system is instantaneously perturbed applying a small electric field: $\delta \nu_{ext}(\mathbf{r}, t) = -k_0 x_\nu \delta(t)$ where $x_\nu = x, y, z$. In this way all frequencies of the system are excited with equal weight, and it is equivalent to give a small momentum $k_0$ to the electrons, so at the time $0^+$ the perturbed wave functions are:

$$\psi_I(\mathbf{r}, t = 0^+) = e^{ik_0 x_\nu} \psi_I(\mathbf{r}, 0)$$  \hspace{1cm} (2.31)
2.3 Dielectric Function

Where \( \psi_i(r, 0) \) is the ground state of the system. Next, the orbitals are propagated in time:

\[
\psi_i(r, t + \delta t) = \mathcal{T} \exp \left\{ -i \int_{t}^{t+\delta t} dt \hat{h}_{KS}(t) \right\} \psi_i(r, t) \tag{2.32}
\]

The absorption spectrum then can be calculated by Eqs. (2.13 and 2.14). Noticing that the perturbation (a delta-function in real time) is a constant function in the frequency domain, we can evaluate the polarizability as:

\[
\alpha_{\nu\nu}(\omega) = -\frac{1}{k_0} \int d\mathbf{r} \delta n(\mathbf{r}, \omega). \tag{2.33}
\]

In this expression \( \delta n(\mathbf{r}, \omega) \) is the Fourier transform of \( n(r, t) - n(r, 0) \) where \( n(r, 0) \) is the ground-state density of the system. Of course according with Eq. (2.14) it is necessary to calculate the polarizability for each spatial direction. With this time-evolution scheme it is also possible to calculate circular dichroism for chiroptical molecules, which is a very powerful tool used for characterization of biomolecules.

In order to do that the main quantity that has to be calculated is the rotatory power strength function \( R(\omega) = R_x(\omega) + R_y(\omega) + R_z(\omega) \) that is obtained by Fourier transform of the time evolution of the angular momentum operator:

\[
L_{\nu}(t) = \sum_i^{\text{occ}} \langle \psi_i \rangle \left( -i(r \times \nabla)_{\nu} \right| \psi_i \rangle. \tag{2.34}
\]

A great advantage of the time dependent scheme, as mentioned above, is that it is not necessary an explicit calculation of unoccupied states, moreover it can be extended to study non linear phenomena and it is also possible to perform nuclear dynamics, eventually driven by high intensity laser fields [Castro 04b] to study laser induced ionization and fragmentation problems.

### 2.3 Dielectric Function

We end this chapter giving the definition for extended systems of the dielectric matrix and the screened coulomb potential that are key ingredient for the quasiparticle and excitonic calculations that will be described in the next chapter. Here we will give a description of these key-quantities starting from a density functional approach, because it has been the starting point of all calculations performed in this thesis. As described above, the response of the charge distribution of an electronic
system to an external perturbation \( \delta w(\mathbf{r}, t) \), is described in linear response theory, by the full polarization function, \( \chi(\mathbf{r}, \mathbf{r}', \omega) \), see Eq. (2.11). We have also defined in Eq. (2.15) the polarization of an independent system \( (\chi_{KS}) \) that link a change in the electron density to a change in the total effective potential, that in the next we indicate with \( \chi^0(\mathbf{r}, \mathbf{r}', \omega) \):

\[
\delta n(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi^0(\mathbf{r}, \mathbf{r}', \omega)V_{tot}(\mathbf{r}', \omega).
\] (2.35)

In DFT framework, the independent particle polarization is accessible from the KS eigenvalues and eigenfunction by Eq. (2.17) and the interacting and non-interacting polarization functions, are connected by Dyson-like equation Eq. (2.18), that written in matrix formalism reads:

\[
\chi = [1 - \chi^0(v + f_{xc})]^{-1} \chi^0
\] (2.36)

In connection with classical electrodynamics we define the inverse dielectric function as a measure of the screening in the system through the ratio between the total and applied potentials:

\[
\epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta V_{tot}(\mathbf{r}, \omega)}{\delta w(\mathbf{r}', \omega)}
\] (2.37)

In order to relate the dielectric function to the microscopic polarizability we consider now a test particle as a probe. The induced charge create a screening and the probe will be only affected by the electrostatic Hartree variation in Eq. (2.16), i.e.:

\[
\delta V_{tot}(\mathbf{r}, \omega) = \delta w(\mathbf{r}, \omega) + \int d\mathbf{r}' \delta n(\mathbf{r}', \omega)v(\mathbf{r}, \mathbf{r}'),
\] (2.38)

where with \( v(\mathbf{r}, \mathbf{r}') \) we have indicated the coulomb potential. Now we can easily relate the dielectric matrix to the polarizability by:

\[
\epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') + \int d\mathbf{r}' v(\mathbf{r}, \mathbf{r}')\chi(\mathbf{r}, \mathbf{r}', \omega)
\] (2.39)

Once introduced the inverse dielectric matrix \( \epsilon^{-1}(\mathbf{r}, \mathbf{r}') \), it is useful to define the dynamically screened Coulomb interaction \( W \):

\[
W(\mathbf{r}, \mathbf{r}', \omega) = \int d\mathbf{r}_1 v(\mathbf{r}, \mathbf{r}_1)\epsilon^{-1}(\mathbf{r}_1, \mathbf{r}', \omega)
\] (2.40)

The interaction function \( W \), take into account the screening and, as we will see later, is a key quantity for quasiparticle and excitonic calculations. Now we can introduce the so called Random Phase Approximation (RPA), that is obtained by
setting the exchange correlation contribution to $\chi$ equal to zero in Eq. (2.36). So in this approximation the dielectric function is obtained by:

$$\epsilon_{RPA}^{-1} = 1 + v(1 - \chi^0 v)^{-1} \chi^0$$  \hfill (2.41a)

$$\epsilon_{RPA} = 1 - v \chi^0$$  \hfill (2.41b)

The Random Phase Approximation is widely used and we have made extensive use of it for the calculation of the screened potential. The dielectric function $\epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$, is a microscopic quantity and in order to relates it to measurable quantities, spatial averages have to be performed. In the case of solids, following Refs. [Adler 62, Wiser 63] the macroscopic dielectric function is related to the inverse of the microscopic dielectric matrix by:

$$\epsilon_M(\omega) = \lim_{q \to 0} \frac{1}{\epsilon^{-1}_{G,G'}(q, \omega)} \bigg|_{G=G'=0}$$  \hfill (2.42)

where we have expressed the microscopic dielectric in momentum space, which is related to real space by a Fourier transform:

$$\epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{(2\pi)^3} \int_{B_z} d\mathbf{q} \sum_{G,G'} e^{i(\mathbf{q}+\mathbf{G}) \cdot \mathbf{r}} \epsilon^{-1}_{G,G'}(\mathbf{q}, \omega) e^{-i(\mathbf{q}+\mathbf{G}) \cdot \mathbf{r}}$$  \hfill (2.43)

where $\mathbf{q}$ lies in the first Brillouin zone and $\mathbf{G}$ are reciprocal lattice vectors. Here we note that Eq. (2.42) requires an inversion of the microscopic dielectric matrix and in general differs from $\lim_{q \to 0} \epsilon_{0,0}(\mathbf{q}, \omega)$. The discrepancy between these two quantity is called **Local Field Effect**. The local field effects take into account microscopic fluctuations induced at atomic scale that arise for the inhomogeneity of the system. The macroscopic dielectric function is then linked to the measurable absorption spectra (ABS) and electron energy loss spectra (EELS) by [Grosso 00]:

$$ABS \equiv \Im \left[ \epsilon_M \right]$$  \hfill (2.44a)

$$EELS \equiv -\Im \left[ \frac{1}{\epsilon_M} \right]$$  \hfill (2.44b)

Note that for finite system we have that absorption spectra is proportional to the dynamical polarizability as seen in Eq. (2.14) and imaginary part of the dielectric function and the loss function coincide [Sottile 05].
3 Many Body Perturbation Theory

The KS-DFT scheme, as presented in the previous chapter, provides very good results for the ground state properties of a huge class of system, but it has also drawbacks: as seen in section (1.2.1), the eigenvalues obtained from the solution of the KS equations, except for the highest occupied, does not have a physical meanings, and when used to calculate gaps of semiconductor or insulator the results are extremely poor, the gaps are underestimated and the quality of the band structures depends strongly on the studied material. In order to obtain physical meaningful gaps we have to go beyond the the DFT scheme and to resort to the quasiparticle (QP) concepts. The quasiparticle energies are given by the energy needed to add (remove) an electron to the system and are experimentally accessible from direct or inverse photo-emission experiments. In this chapter we will briefly describe this concepts by the Many Body Perturbation Theory (MBPT), introducing the Green Function formalism, the Self Energy concept and the GW approximation, and we remind the reader to the following books and article of many particle physics [Fetter 81, Hedin 69, Gross 91] for a deeper discussions. Then in section (3.4) we will see how to include the electron-hole attraction effects in the macroscopic dielectric function going beyond the GW approximation. Last, in section (3.5) we will combine the MBPT with the TDDFT for obtaining an exchange-correlation kernel that includes both the quasiparticle energies and the electron-hole attraction effects that has been extensively used chapter (7).

3.1 Quasiparticle formulation

In section (1) we have seen that in the Kohn-Sham scheme the response of a system of interacting electrons to an external potential is mapped into a system of non-interacting electrons responding to an effective potential (KS potential). In Many Body Perturbation Theory we start from the idea that an electron in an interacting
system perturbs the particles in its proximity and can be tough as a particle moving through the system, surrounded by a cloud of other particles that are being pushed out of the way or dragged along by its motions, so that the entire entity moves like a weakly interacting particle. The entity particle plus screening cloud is called quasiparticle. So, similarly as the Kohn-Sham scheme, the interacting “bare” particle problems can be described via weakly interacting quasiparticles as they interact via a screened potential rather than the bare coulomb potential. The advantage of such description permits to perform a perturbative expansion with respect the quasiparticle interaction. Note that the quasiparticles states are not eigenstates of the N-body Hamiltonian and therefore they have a finite lifetime.

One particle Green’s function

The quantity that describe the propagation of one particle through the system is the one particle Green’s function. It contains the information on energy and lifetimes of the quasiparticle, and also on the ground state energy of the system and the momentum distribution. The one particle Green’s function is defined as:

\[
G(x_1, t_1, x_2, t_2) = -i\langle \Psi_N | T[\psi_H(x_1, t_1)\psi_H^\dagger(x_2, t_2)] | \Psi_N \rangle,
\]

(3.1)

Here we use the abbreviation \( x = (x, t) = (r, \sigma, t) \). \( \Psi_N \) is the Heisenberg ground state vector of the interacting N-electron system satisfying the Schrödinger equation \( \hat{H} | \Psi_N \rangle = E | \Psi_N \rangle \), \( \psi_H \) and \( \psi_H^\dagger \) are respectively the annihilation and creation field operator and T is the Wick time ordering operator. Explicitly:

\[
\begin{align*}
\psi_H(x, t) &= e^{i\hat{H}t}\psi(x)e^{-i\hat{H}t} \quad (3.2a) \\
\psi_H^\dagger(x, t) &= e^{-i\hat{H}t}\psi^\dagger(x)e^{i\hat{H}t} \quad (3.2b)
\end{align*}
\]

and the field operator satisfy the anti-commutation relation:

\[
\begin{align*}
\{ \psi_H(x), \psi_H^\dagger(x') \} &= \delta(x - x') \quad (3.3a) \\
\{ \psi_H(x), \psi_H(x') \} &= \{ \psi_H^\dagger(x), \psi_H^\dagger(x') \} = 0 \quad (3.3b)
\end{align*}
\]

and:

\[
T[\psi_H(x_1, t_1)\psi_H^\dagger(x_2, t_2)] = \begin{cases} 
\psi_H(x_1, t_1)\psi_H^\dagger(x_2, t_2) & \text{if } t_1 > t_2 \\
-\psi_H(x_2, t_2)\psi_H^\dagger(x_1, t_1) & \text{if } t_1 < t_2 
\end{cases} \quad (3.4)
\]
The Hamiltonian \( \hat{H} = \hat{T} + \hat{W} + \hat{V} \) of Eq. (1.1) in the second quantization formalism now reads:

\[
\hat{T} = \int d\mathbf{x} \psi^+_H(x) \left[ -\frac{1}{2} \nabla^2 \right] \psi_H(x) \quad (3.5a)
\]

\[
\hat{W} = \int d\mathbf{x} \psi^+_H(x) w(x) \psi_H(x) \quad (3.5b)
\]

\[
\hat{V} = \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \psi^+_H(x) \psi^+_H(x') v(\mathbf{r}, \mathbf{r}') \psi_H(x') \psi_H(x) \quad (3.5c)
\]

From this definition we can see that the Green function \( G(x_1, x_2) \) describes the probability amplitude for the propagation of an electron (hole) from position \( \mathbf{r}_2 \) at \( t_2 \) to \( \mathbf{r}_1 \) at time \( t_1 \) for \( t_1 > t_2 \) (\( t_1 < t_2 \)). If now we introduce the complete set of the eigenstates of the Hamiltonian \( H \), for the (N+1) and (N-1) particle systems and we perform a Fourier transform in energy space we obtain:

\[
G(x_1, x_2; \omega) = \sum_s \frac{f_s(x_1) f^*_s(x_2)}{\omega - \varepsilon_s + i\eta \text{sgn}(\varepsilon_s - \mu)} \quad (3.6)
\]

where \( \mu \) is the chemical potential,

\[
\varepsilon_s = \begin{cases} 
E_s^{(N+1)} - E_N^{(N)} & \text{for } \varepsilon_s \geq \mu \\
E_N^{(N)} - E_s^{(N-1)} & \text{for } \varepsilon_s < \mu
\end{cases} \quad (3.7)
\]

where for the total energies we have used the notation of section (1.2.1) and with the subscript \( s \) we indicate the quantum label of the states of the N+1 (N-1) system.

The amplitudes \( f_s(x) \) are defined as:

\[
f_s(x) = \begin{cases} 
\langle \Psi_N | \psi(x) | \Psi_{N+1,s} \rangle & \text{for } \varepsilon_s \geq \mu \\
\langle \Psi_{N-1,s} | \psi(x) | \Psi_N \rangle & \text{for } \varepsilon_s < \mu
\end{cases} \quad (3.8)
\]

We see from the expression (3.6) that the Green function has the poles at the electron addition (removal) energies and describes quasiparticle excitations. By taking the imaginary part of Eq. (3.6) we have the so-called spectral function:

\[
A(x_1, x_2; \omega) = \frac{1}{\pi} |\Im G(x_1, x_2; \omega)| = \sum_s f_s(x_1) f^*_s(x_2) \delta(\omega - \varepsilon_s) \quad (3.9)
\]

\( A(x_1, x_2; \omega) \) is a superposition of delta functions with weights given by the amplitudes \( f_s(x) \) centered at each of the one particle excitation energies \( \varepsilon_s \). In the cases where an appreciable fraction of the weight spectral function \( A(x_1, x_2; \omega) \) goes into
Figure 3.1: Schematic representation of non-interacting and interacting spectral function for a hole. The non-interacting spectral function centered at $\omega = \epsilon_{ni}$ broads and shifts to $\omega = \epsilon_{qp}$ when the interaction is switched on, and another satellite peak appears at $\omega = \epsilon_{sat}$. The width of the QP peak reflects the finite lifetime of the excitation.

A well defined and narrow peaks, reflecting the existence of an high-probable one-electron excitations, it can be explained approximately in terms of a particle-like behavior, and in this case we speak about quasiparticle states or elementary excitations. Of course we can not assign this peak to an independent electron (hole) added (removed) to the system because the Coulomb interaction. In the case of non-interacting electrons, the eigenstates can be described by single-particle orbitals $\phi_j(\mathbf{r})$ and the matrix element of the spectral function $A_{ij}$ in this basis representation, reduces to a delta function centered in the one-electron orbital energy.

$$A^{\text{non-interact}}_{ij}(\omega) = \langle \phi_i | A(x_1, x_2; \omega) | \phi_j \rangle = \delta_{ij} \delta(\omega - \epsilon_i)$$  \hspace{1cm} (3.10)

where $\epsilon_i$ is the eigenvalues associated to $\psi_i$. When the interaction is switched-on the delta function change in position, broaden and loses spectral weight, which is redistributed in a more complicated structure (the QP peak) and eventually other minor peaks (satellites), see Fig. 3.1. We see more in detail this one-electron picture by introducing the Self Energy operator $\Sigma$. 

The Self-Energy $\Sigma$

An implicit definition of $\Sigma$ can be given from the equation of motion of the one particle Green’s function which involves the two-particle Green’s function [Hedin 69]. The self-energy allows to close formally the hierarchy of equations of motion of higher order Green functions. We introduce the Self Energy through the Dyson equation:

$$G(x_1, x_2) = G_H(x_1, x_2) + \int dx_3 dx_4 G_H(x_1, x_3) \Sigma(x_3, x_4) G(x_4, x_2)$$  \hspace{1cm} (3.11)$$

where $G_H$ is the Hartree Green function of the non-interacting system, solution of the equation:

$$[\omega - \hat{h}_0(x_1)]G_H(x_1, x_2; \omega) = \delta(x_1 - x_2)$$  \hspace{1cm} (3.12)$$

here $\hat{h}_0(x)$ is the one-electron Hamiltonian: $\hat{h}_0(x) = -\nabla^2/2 + w(x) + V_H(x)$ under the total average potential (external potential plus classical Hartree potential). From Eqs (3.11) and (3.12) it is clear that the operator $\Sigma$ contain all the exchange and correlation many body effects:

$$[\omega - \hat{h}_0(x_1)]G(x_1, x_2; \omega) = \delta(x_1 - x_2) + \int dx\Sigma(x_1, x; \omega) G(x, x_2; \omega)$$  \hspace{1cm} (3.13)$$

The complicate many-body character of the Green’s function $G$ arise from the Energy dependence in Eq. (3.13). Expressing the Green function in a base of energy dependent wave functions $\phi_i(x, \omega)$, that form an orthonormal and complete set for each $\omega$ as:

$$G(x_1, x_2) = \sum_i \frac{\phi_i(x_1, \omega)\phi_i^*(x_2, \omega)}{\omega - E_i(\omega)}$$  \hspace{1cm} (3.14)$$

provided that the complex wave-functions $\phi_i(x, \omega)$ and energies $E_i(\omega)$ are solution of the equation:

$$\hat{h}_0(x)\phi_i(x, \omega) + \int dx'\Sigma(x, x'; \omega) \phi_i(x', \omega) = E_i(\omega)\phi_i(x, \omega)$$  \hspace{1cm} (3.15)$$

Because $\Sigma$ is a non-hermitian operator the energies $E_i(\omega)$ are in general complex and the imaginary part gives the lifetime of the excitation. If the energy spectrum presents sharp peaks as illustrated in the previous paragraph $E_i(\omega) \approx E^{QP}_i$ we arrive at the quasiparticle equation:

$$\hat{h}_0(x)\phi^{QP}_i(x) + \int dx'\Sigma(x, x'; E^{QP}_i) \phi^{QP}_i(x') = E^{QP}_i \phi^{QP}_i(x)$$  \hspace{1cm} (3.16)$$

We can see from this equation that the qp-equation has a resemblance to the KS equation (1.16a) where the non local and energy dependent Self Energy $\Sigma$ plays
the role of the exchange and correlation potential \( v_{xc} \), but while the xc potential is part of the potential of the fictitious non interacting system, \( \Sigma \) may be tough as the potential felt by an added (removed) electron to (from) the interacting system. From the solution Eq. (3.16), expanding \( \Sigma_i(\omega) = \langle \phi_i^{QP}|\Sigma(\omega)|\phi_i^{QP} \rangle \) around the value \( \omega = E_i^{QP} \) we can calculate the Green function and the spectral function (3.9) as:

\[
G_i(\omega) = \langle \phi_i^{QP}|G(\omega)|\phi_i^{QP} \rangle \simeq \frac{Z_i}{\omega - (\Re(E_i^{QP}) - i\Im(E_i^{QP}))}
\]

(3.17)

where \( Z_i \) is the so-called renormalization factor defined as:

\[
Z_i^{-1} = 1 - \frac{\partial \Sigma_i(\omega)}{\partial \omega} \bigg|_{\omega=E_i^{QP}}
\]

(3.18)

and gives the portion of the spectral weight under the quasiparticle peak. We see that if \( \Im(E_i^{QP}) \) is small the spectral function will present a well defined peak centered around \( \Re(E_i^{QP}) \).

### 3.2 Hedin’s Equations

Until now we have seen how it is possible to calculate energy and lifetimes of quasiparticle excitation solving Eq. (3.16). Of course before that we have to know how is made the operator \( \Sigma \), that have of course be approximated. The Many Body Perturbation Theory gives us a practical scheme in order to solve such task. As perturbation we will not consider the bare coulomb potential, \( V \), but results more natural to consider the screened coulomb potential \( W \) introduced in Eq. (2.40) that has reduced strength with respect the bare potential, and we will write the Self Energy as a perturbation series in terms of \( W \). A systematic way to construct exactly \( \Sigma \) was proposed by Hedin [Hedin 65, Hedin 69] and consists of a set of five Dyson like equations:

\[
P(12) = -i \int d(34)G(13)G(41^+)\Gamma(34, 2)
\]

(3.19a)

\[
W(12) = V(12) + \int d(34)W(13)P(34)V(4, 2)
\]

(3.19b)

\[
\Sigma(12) = i \int d(34)G(14)W(1^+3)\Gamma(42, 3)
\]

(3.19c)

\[
G(12) = G^0(12) + \int d(34)G^0(13)\Sigma(34)G(42)
\]

(3.19d)

\[
\Gamma(12, 3) = \delta(12)\delta(13) + \int d(4567) \frac{\partial \Sigma(12)}{\partial G(45)}G(46)G(75)\Gamma(67, 3)
\]

(3.19e)
3.3 The GW approximation

where we used the notation \(1 \equiv (x_1, t_1)\). Above \(P\) is the irreducible polarization function, \(\Gamma\) is the so called vertex function and \(G^0\) coincide with the Hartree Green function (see Eq. (3.11)) Note here that the irreducible polarization function \(P\), represents the variation of the induced density with respect to a variation of a classical total potential (external plus Hartree) and differs from the polarization function defined in section (2.3) \(^1\) and it is related to the dielectric function by \(^2\):

\[
\epsilon(12) = \delta(12) - \int d(3)V(13)P(32) \quad (3.20)
\]

We can here recognize that if we consider \(\Sigma = 0\) in Eq. (3.19e), we get \(P^0(12) = -iG^0(12)G^0(21^+)\), in this case \(P^0\) and \(\chi^0\) coincide and Eq. (3.20) is the RPA dielectric function of Eq. (2.41b).

3.3 The GW approximation

A method to solve this set of equation was proposed by Hedin, by starting the iterative solution starting \(\Sigma = 0\) (Hartree approximation). This approximations yields to \(\Gamma(12, 3) = \delta(12)\delta(13)\). The others expressions of Eq. (3.19) becomes in first iteration:

\[
P^0(12) = -iG^0(12)G^0(21^+) \quad (3.21a)
\]

\[
W^0(12) = V(12) + \int d(34)W^0(13)P^0(34)V(4, 2) \quad (3.21b)
\]

\[
\Sigma(12) = iG^0(12)W^0(1+2) \quad (3.21c)
\]

The GW approximation \(^3\) consists in stopping at the first step of the iteration, so in neglecting the vertex function and calculating the \(\Sigma\) by Eq. (3.21) and then solve the quasiparticle equation (3.16). Substantially from Eq. (3.21) we can recognize that \(G^0\) is just the Hartree Green’s function, the polarizability \(P^0\) is the independent particle polarization and gives the Adler Wiser polarization function, \(W^0\) is the RPA

\(^1\) In Eq. (2.11) we have defined the reducible response, i.e. the variation of the induced density with respect the variation of the external field.

\(^2\) Note that Eq. (3.19b) can be written as: \(W = e^{-1}V\) linking the screened Coulomb to the bare Coulomb.

\(^3\) Here we describe the non self-consistent GW approximation, that is the approach we have adopted in this thesis. For a general overview on the GW approximation see:[Aryasetiawan 98, Aulbur 00a]
screened potential, and $\Sigma$, now updated, is just the product of $G$ and $W$ hence the name of the approximation. A better choice for the starting Green Function $G^0$ than the Hartree Green’s function, is to use the Green’s Function of the non interacting KS system $G_{KS}$, which already contains an attempt to include the exchange and correlation effects.

$$G_{KS}(\omega)(x, x') = \sum_i \frac{\psi_i^{KS}(x)\psi_i^{KS*}(x')}{\omega - \epsilon_i^{KS} - i\eta \text{sgn}(\mu - \epsilon_i^{KS})} \quad (3.22)$$

constructed with the eigenfunctions $\psi_i^{KS}$ and eigenvalues $\epsilon_i^{KS}$ obtained from the solution of the KS equations (8.37). In many materials the KS and the QP eigenfunctions are quite identical. This fact permits to use the KS eigenfunction to calculate both the dielectric matrix and the matrix elements of $\Sigma$ and it is not even necessary to solve Eq. (3.16). In practice we calculate the $G$ in Eq. (3.22) and $\chi^0$ in Eq. (2.17) to calculate $\epsilon^{-1}$ from Eq. (2.41a) using the KS wave-functions and eigenvalues, and we expand to first order Taylor series the Self Energy (Eq.3.21c) around the KS eigenvalues:

$$\langle \Sigma(E_i^{QP}) \rangle \simeq \langle \Sigma(\epsilon_i^{KS}) \rangle + \left. \left\langle \frac{\partial \Sigma(\omega)}{\partial \omega} \right\rangle_{\omega=\epsilon_i^{KS}}(E_i^{QP} - \epsilon_i^{KS}) \right\rangle \quad (3.23)$$

The quasiparticle energies in first order perturbation theory results to be:

$$E_i^{QP} = \epsilon_i^{KS} + \frac{\langle \Sigma(\epsilon_i^{KS}) \rangle - \langle V_{\text{xc}}^{LDA}\rangle_{\epsilon_i^{KS}}}{1 - \left. \left\langle \frac{\partial \Sigma(\omega)}{\partial \omega} \right\rangle_{\omega=\epsilon_i^{KS}} \right\rangle} \quad (3.24)$$

The GW approximation furnish very good results in agreement with experiments for the calculation of band structures and photo-emission spectra of many semiconductors and insulator [Hybertsen 86, Godby 88, Rubio 93, Zakharov 94]. In spite of such success, if we want to calculate absorption spectra, just substituting the quasi particle energies to the KS energies in Eq. (3.22) it will yield very poor results, giving in general a blue-shift with respect the experimental values. The reason of such failure is due to the nature of the GW approximation. If we look at the expression of the polarization Eq. (3.21a) which describe the propagation of an electron ($G(12)$) and an hole ($G(21)$) preventing any interaction between them. The GW approximation describes properly excitations that involve a change in the number of the electrons in the system, addition or remotion of an electron, while the absorption involves excitations where the number of particles is constant: an electron in an occupied state, is promoted to an empty state, leaving an hole. Such process is a two particle excitations and for a proper description of such excitation it is needed to include the vertex function $\Gamma$ in Eq. (3.19a) as we will see in the next section.
3.4 Two particle effects

In this section we will give a brief description of how include in the macroscopic dielectric function $\epsilon_M$ (Eq. (2.42)) the electron-hole attraction (excitonic effects). This is done going beyond the GW approximation by taking a second iteration in the Hedin’s equation (3.19). Here we will derive the main equation to describe the two-particles excitations: the Bethe-Salpeter equation (BS), and we will furnish the scheme to solve it adopted in this thesis. For a general review we refer to the references [[Strinati 88, Onida 02]].

Second iteration of Hedin’s equations

If we perform a second iteration of the Hedin’s equation, now using $\Sigma = iGW$ as starting point, we get the following equation for the vertex function $\Gamma$

$$\Gamma(12, 3) = \delta(12)\delta(13) + iW(1^+, 2) \int d(45)G(14)G(52)\Gamma(45, 3)$$  \hspace{1cm} (3.25)

where we considered $\delta \Sigma / \delta G = iW$ neglecting the term $iG\delta W / \delta G$ that is supposed to be small [Hanke 80, Strinati 84]. Now we introduce a four point polarization function $P(1, 2; 3, 4)$ such that the polarization $P(1, 2)$ of Eq. (3.19a) is obtained by as $P(1, 1; 2, 2)$ and we define a four point screened interaction $W(1, 2; 3, 4) = W(1, 2)\delta(13)\delta(24)$. In this manner from Eq. (3.19a) and (3.25) we get a Dyson like equation for the four-point polarization:

$$P(1, 2; 3, 4) = P^0(1, 2; 3, 4) - \int d(5678)P(1, 2; 5, 6)W(5, 6; 7, 8)P^0(7, 8; 3, 4)$$  \hspace{1cm} (3.26)

From the solution of Eq. (3.26) it is possible to calculate the microscopic dielectric function with Eq. (3.20) and subsequently the macroscopic dielectric matrix via Eq. (2.42). Here following Ref.[[Albrecht 99, Onida 02]] we define in matrix form a new polarization function $\overline{P}$ as:

$$\overline{P} = P + P\overline{\nu}\overline{P}$$  \hspace{1cm} (3.27)

where $\overline{\nu}$ is the bare coulomb potential without the long range term that in reciprocal space reads:

$$\overline{\nu}_G(q) = \begin{cases} 0, & G = 0 \\ v_G(q), & G \neq 0 \end{cases}$$  \hspace{1cm} (3.28)
It can be demonstrated [Albrecht 99] that this new polarization function $P$ is related to the macroscopic dielectric function by:

$$\epsilon_M(\omega) = 1 - \lim_{q \to 0} [v_0(q) P_{00}(q, \omega)]$$

(3.29)

or equivalently:

$$\epsilon_M(\omega) = 1 - \lim_{q \to 0} \left[ v_0(q) \int d\mathbf{r} d\mathbf{r}' e^{-i\mathbf{r} \cdot \mathbf{q}} P(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}'', \omega) \right]$$

(3.30)

Inserting Eq. (3.26) in Eq. (3.27) we obtain the so-called Bethe Salpeter Equation (BS) that in matrix form reads::

$$\overline{P} = P^0 + P^0 K \overline{P}$$

(3.31)

The Kernel $K$ of the BS equation:

$$K(1, 2; 3, 4) = -i\delta(1, 2)\delta(3, 4)\pi(1, 3) + i\delta(1, 3)\delta(2, 4)W(1, 2)$$

(3.32)

is composed of two terms: The first one is called the exchange term, while the second one, that is the variation of the Self energy with respect the single particle Green’s function is called direct-term. In the $GW$ approximation it is the screened coulomb potential. We note here that if we replace the screened coulomb potential by the bare coulomb potential, the BS equation reduces to the time dependent Hartree Fock equation.

**Effective two particle equation**

In the last section we have shown how to include the electron-hole attraction in the macroscopic dielectric function, introducing a four point polarizability that could be calculated solving the Dyson-like equation Eq. (3.31) through an inversion. This is a very cumbersome procedure, so here, we show how to reduce the calculation of the 4-point polarization function to an effective eigenvalue problem to be solved by diagonalization. The main idea is to use a basis of KS Bloch function pairs $\phi_n(\mathbf{r})\phi_{n'2}(\mathbf{r})$ and use the spectral representation for the inversion. First of all we consider the propagation and the interaction of the two particle simultaneous and instantaneous. In this way we reduce the four time coordinate to just one. In the next we will use the notation $\mathbf{x}_1 \to \{\mathbf{r}_1, \sigma_1\}$, so the time coordinate it is not included anymore in the index, and performing a Fourier Transform in energy space we will
have $\mathcal{P}(1, 2; 3, 4) \rightarrow \mathcal{P}(x_1, x_2; x_3, x_4|\omega)$. The change of basis in transition space is performed by the relation:

$$
\mathcal{P}_{(n_1, n_2)(n_3, n_4)} = \int dx_1 dx_2 dx_3 dx_4 \mathcal{P}(x_1, x_2; x_3, x_4) \phi_{n_1}(x_1) \phi_{n_2}^*(x_2) \phi_{n_3}^*(x_3) \phi_{n_4}(x_4)
$$

(3.33)

In the transition space the non-interacting polarizability reads:

$$
P^0_{(n_1, n_2)(n_3, n_4)} = \frac{(f_{n_2} - f_{n_1}) \delta_{n_1, n_3} \delta_{n_2, n_4}}{\epsilon_{n_2} - \epsilon_{n_1} - \omega - i\eta}
$$

(3.34)

where with $f_n$ we have indicate the occupation number and $\eta$ is a positive infinitesimal. Now we define the excitonic Hamiltonian as:

$$
H_{exc}^{(n_1, n_2)(n_3, n_4)} = (\epsilon_{n_2} - \epsilon_{n_1}) \delta_{n_1, n_3} \delta_{n_2, n_4} + i(f_{n_2} - f_{n_1}) K_{(n_1, n_2)(n_3, n_4)}
$$

(3.35)

from Eq. (3.31) can be shown that the polarizability $\mathcal{P}$ can be expressed as:

$$
\mathcal{P}_{(n_1, n_2)(n_3, n_4)} = \left[H_{exc} - I_\omega\right]^{-1}_{(n_1, n_2)(n_3, n_4)} (f_{n_4} - f_{n_3})
$$

(3.36)

where $I$ is the identity matrix $I = \delta_{n_1, n_3} \delta_{n_2, n_4}$. In order to solve the inversion we use the spectral representation, namely:

$$
\left[H_{exc} - I_\omega\right]^{-1}_{\lambda, \lambda'} = \sum_{\lambda, \lambda'} |\lambda\rangle S^{-1}_{\lambda, \lambda'} \langle \lambda'|_{E_{\lambda} - \omega}
$$

(3.37)

where with $|\lambda\rangle$ and $E_{\lambda}$ we have indicated the eigenvalues and eigenvector of $H_{exc}^{(n_1, n_2)(n_3, n_4)}$:

$$
H_{exc}^{(n_1, n_2)(n_3, n_4)} |\lambda\rangle = E_{\lambda} |\lambda\rangle
$$

(3.38)

and $S_{\lambda, \lambda'}$ is the overlap matrix:

$$
S_{\lambda, \lambda'} = \langle \lambda'|\lambda\rangle
$$

(3.39)

Note that Eq. (3.37) holds for a general non Hermitian matrix. Explicitly we have defined an effective two-particle Schrödinger equation:

$$
H_{(n_1, n_2)(n_3, n_4)}^{exc} A^{(n_1, n_2)} = E_{\lambda} A^{(n_1, n_2)}
$$

(3.40)

that can be solved by diagonalization. This equation couples the different two particle configurations and the coefficients $A^{(n_1, n_2)}_{\lambda}$ of the state $|\lambda\rangle$ permits to identify the character of each excitation. The exciton amplitude is given by:

$$
\Psi_{\lambda}(x_1, x_2) = \sum_{n_1, n_2} A^{(n_1, n_2)}_{\lambda} \phi_{n_1}^*(x_1) \phi_{n_2}(x_2)
$$

(3.41)
Moreover from the eigenvectors and eigenvalues of Eq. (3.40) we can calculate from Eqs. (3.29), (3.36), (3.37) the macroscopic dielectric matrix by:

\[
\epsilon_M(\omega) = 1 - \lim_{q \to 0} \left\{ v_0(q) \sum_{\lambda,\lambda'} \sum_{n_1, n_2} \langle n_1 | e^{-i q r} | n_2 \rangle \frac{A^{(n_1, n_2)}_{\lambda}}{E_{\lambda} - \omega - i\eta} \times \right. \\
\left. \times S_{\lambda,\lambda'}^{-1} \sum_{n_3, n_4} \langle n_3 | e^{i q r} | n_4 \rangle A^{*(n_3, n_4)}_{\lambda} (f_{n_4} - f_{n_3}) \right\} 
\]

(3.42)

### Structure of the Excitonic Hamiltonian

In this section we examine the structure of the excitonic Hamiltonian Eq. (3.35) more in detail. We indicate with the letter \( v \) and \( c \) respectively the occupied and empty states and we omit the index \( k \) associated to the vertical transition \( v \rightarrow c \) that have to be considered when solids are studied. Eq. (3.35) has the following structure:

\[
H_{exc} = \begin{pmatrix}
\{v'c'\} & \{c'v'\} & \{v''v'\} & \{v'\bar{v}'\} \\
\{vc\} & H_{exc, res}^{(v,c)(v',c')} & K^{(v,c)(v',c')} & K^{(v,c)(v',\bar{c}')} \\
\{v\bar{v}\} & -[K^{(v,c)(v',c')}]^* & -H_{exc, res}^{(v',c')(v,c')} & (\epsilon_\bar{v} - \epsilon_v)\delta_{v,v'}\delta_{\bar{v}',\bar{v}} \\
\{c\bar{c}\} & 0 & 0 & (\epsilon_\bar{c} - \epsilon_c)\delta_{c,c'}\delta_{\bar{c}',\bar{c}} \\
\end{pmatrix}
\]

(3.43)

From Eq. (3.36) it can be shown that not all the terms contribute to the macroscopic dielectric function, and the relevant part of the excitonic Hamiltonian reduces to only the terms between occupied and unoccupied pairs:

\[
H_{exc} = \left( \begin{array}{cc} H_{exc, res}^{(v,c)(v',c')} & K^{coupl}^{(v,c)(v',c')} \\ -[K^{coupl}^{(v,c)(v',c')}]^* & -[H_{exc, res}^{(v',c')(v,c')}]^* \end{array} \right)
\]

(3.44)

The two diagonal blocks involves only positive and negative frequency transitions and are called respectively resonant and anti-resonant parts, while the off-diagonal block mix positive and negative transition and we call them coupling part. From Eq. (3.35) and Eq. (3.32) we can write the different terms of the Hamiltonian explicitly. We split the resonant part in three terms:

\[
H_{exc, res}^{(v,c)(v',c')} = H_{dia}^{(v,c)(v',c')} + K^{x}^{(v,c)(v',c')} + K^{d}^{(v,c)(v',c')}
\]
that have the forms:

\[ H_{(v,c)(v',c')}^{\text{dia}} = (\epsilon_c - \epsilon_v) \delta_{vv'} \delta_{cc'} \]  
\[ K_{x(v,c)(v',c')}^{x} = \int dx \int dx' \phi^*_c(x) \phi_v(x) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{c'}(x') \phi^*_v(x') \]  
\[ K_{d(v,c)(v',c')}^{d} = -\int dx \int dx' \phi^*_c(x) \phi_{c'}(x) \int d\mathbf{r}_1 \epsilon^{-1}(\mathbf{r}, \mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}'|} \phi_v(x') \phi^*_v(x') \]  

In the diagonal term the independent-particle energies \( \epsilon \) are the quasiparticle energies from a GW calculation. In the direct term \( K^d \) the dynamical effects in the screening are neglected, and the static dielectric matrix is calculated in RPA framework Eq. (2.41a). With \( K^x \) we have indicated the so-called exchange term.\(^4\) Similarly the coupling term can be split as:

\[ K_{(v,c)(c',v')}^{\text{coupl}} = K_{(v,c)(c',v')}^{x} + K_{(v,c)(c',v')}^{d} \]  

Looking at the structure of each term results that the resonant part itself is an Hermitian matrix: \((H_{\text{exc, res}}^{\text{exc, res}})^* = (H_{\text{exc, res}}^{\text{exc, res}})^T\), while the coupling part alone is symmetric:

\(^4\) In section (5.4.5) we will derive a similar expression of the Hamiltonian, for the TDDFT, anyway the two equation have a different structure due to the change in the indexes \( \{vc'\} \rightarrow \{c'v\} \) in the direct term.
$K^{\text{coulpl}} = (K^{\text{coulpl}})^T$. Until now we do not have included the spin structure of the of the BS. Under the assumption that the spin-orbit interaction is negligible compared with the electron-hole interaction, we can classify the single-particle states as spin-up and spin-down states. Within this assumption the electron-hole pair space until now indicated as $\{vc\}$ consists of four subspaces: $\{v \uparrow c \uparrow\}, \{v \uparrow c \downarrow\}, \{v \downarrow c \uparrow\}, \{v \downarrow c \downarrow\}$. If now we look at the excitonic Hamiltonian in this subspace we obtain from Eq. (3.45) for the resonant part:

$$H_{\text{res}}^{\text{exc}} = \begin{pmatrix}
\{v \uparrow c \uparrow\} & \{v' \uparrow c' \uparrow\} & \{v' \downarrow c' \downarrow\} & \{v' \downarrow c' \uparrow\} \\
\{v \uparrow c \downarrow\} & 0 & H^{\text{dia}} + K^d & 0 \\
\{v \downarrow c \uparrow\} & 0 & 0 & H^{\text{dia}} + K^d \\
\{v \downarrow c \downarrow\} & K^x & 0 & 0 & H^{\text{dia}} + K^d + K^x
\end{pmatrix}$$

So in the assumption of weak spin-orbit interaction this Hamiltonian can be decoupled into spin-singlet solutions and spin-triplet solutions, and the BS can be solved separately:

$$\text{Singlet} \quad \frac{1}{\sqrt{2}}(v \uparrow c \uparrow - v \downarrow c \downarrow) \quad H^{\text{exc}} = H^{\text{dia}} + K^d + 2K^x$$

$$\text{Triplet} \quad \begin{cases}
v \uparrow c \uparrow \\
v \downarrow c \downarrow \\
\frac{1}{\sqrt{2}}(v \uparrow c \uparrow + v \downarrow c \downarrow)
\end{cases} \quad H^{\text{exc}} = H^{\text{dia}} + K^d$$

(3.47)

In the same manner we obtain for the coupling part:

$$K^{\text{coulpl, singlet}}_{(v,c)(c',v')} = K^d_{(v,c)(c',v')} + 2K^x_{(v,c)(c',v')}$$

$$K^{\text{coulpl, triplet}}_{(v,c)(c',v')} = K^d_{(v,c)(c',v')}$$

Of course in the cases where the spin-orbit coupling cannot be neglected the classification of the single state in spin-up spin-down states is not valid anymore. The singlet and triplet configurations are mixed and the full spin structure have to be included in the Bethe-Salpeter Hamiltonian, but it is not the case for the systems treated in this thesis. We see that the exchange term $K^x$ that involve the bare Coulomb potential Eq. (3.32) controls the splitting between spin-singlet and spin-triplet excitations. The direct term $K^d$ involve the screened Coulomb interaction $W$ produces the attractive electron-hole interaction and is the responsible for the formation of bound electron-hole states, called excitons. In Fig(3.2) are sketched the energy levels and interactions passing from the DFT calculation to the BS solutions through the GW approximations for the quasiparticle energies.
3.5 Combining MBPT and TDDFT

The solution of the Bethe Salpeter equation described above reproduces very well the experimental spectra of semiconductor and insulator. However looking at the excitonic matrix we see that the dimension of the matrix increases with the number of the valence and conduction band, and the \( k \) sampling needed to sample the Brillouin zone in the case of solids. Moreover we have seen that the BS polarization is a four-point function at difference of the TDDFT polarization that is a two-point function. Anyway has said before the TDDFT, at least in the ALDA approximation works very well for finite systems while fails to reproduce excitonic properties of infinite systems. From this consideration it is clear that will be desirable to have a TDDFT kernel \( f_{xc} \) that mimics the results of the BS. In this section we see how to construct a TDDFT kernel. Here we follow the derivation done in Ref. [Marini 03].

The sought \( f_{xc} \) is obtained by imposing TDDFT to reproduce the perturbative expansion of the BS in terms of the screened Coulomb interaction at any order. We start by the TDDFT equation for the irreducible response function \( P_{TDDFT}^{G,G'}(q,\omega) \) in reciprocal space \(^5\):

\[
P_{TDDFT}^{G,G'}(q,\omega) = P^0(q,\omega) + P^0(q,\omega) f_{xc}(q,\omega) P_{TDDFT}^{G,G'}(q,\omega) \tag{3.48}
\]

In this equation \( P^0(q,\omega) \) is the Kohn-Sham response function, i.e. the Fourier transform of Eq. (2.17), and all the quantities are two-point matrices in reciprocal space and the indexes \( \{G,G'\} \) have been omitted. The reducible response function is related to the dielectric function via Eq. (3.20). Now we make the connection with the MBPT first approximating the \( P^0 \) function with the independent quasiparticle response function, i.e substituting the \( KS \) energies in Eq. (2.17) with the \( QP \) energies calculated in GW framework. Next we make the hypothesis that there exist a TDDFT kernel \( f_{xc} \) that reproduce the BS results [Adragna 03] i.e.:

\[
P_{TDDFT}^{G,G'}(q,\omega) = P_{BS}^{G,G'}(q,\omega) \tag{3.49}
\]

where \( \Omega \) is the system’s volume and we have introduced the index \( K = (\epsilon, v, k) \) to describe the electron-hole space. The oscillator \( \Phi_K \) are given by \( \Phi_K(q, G) = \)

---

\(^5\) The transformation to reciprocal space is made analogously to Eq. (2.43). Note that in Eq. (2.18) we have written the TDDFT equation for the reducible response function in real space.
\[ \langle \mathbf{k} | e^{i(q+G) \cdot r} | v \mathbf{k} - \mathbf{q} \rangle. \]

Here, \( P_{\mathbf{K}_i, \mathbf{K}_2}(\mathbf{q}, \omega) \) is the solution of Eq. (3.26) in transition space, that reads:

\[ P^{BS}_{\mathbf{K}_1, \mathbf{K}_2}(\mathbf{q}, \omega) = P_{\mathbf{K}_1, \mathbf{K}_2}^0(\mathbf{q}, \omega) - \frac{\Pi_{\mathbf{K}_1, \mathbf{K}_2}(\mathbf{q})}{W_{\mathbf{K}_1, \mathbf{K}_2}(\mathbf{q})} P^{BS}_{\mathbf{K}_1, \mathbf{K}_2}(\mathbf{q}, \omega) \]  

(3.50)

where \( P_{\mathbf{K}_1, \mathbf{K}_2}^0 \) is given by Eq. (3.34) and

\[ W_{\mathbf{K}_1, \mathbf{K}_2}(\mathbf{q}) = \langle c_1 \mathbf{k}_1, v_2 \mathbf{k}_2 - \mathbf{q} | W(\mathbf{r}_1, \mathbf{r}_2) | c_2 \mathbf{k}_2, v_1 \mathbf{k}_1 \rangle \]  

(3.51)

Note that here we have reduced to the resonant part of \( P \). Writing \( P^{TDDFT}(\mathbf{q}, \omega) = P^0(\mathbf{q}, \omega) + \delta P(\mathbf{q}, \omega) \) Eq. (3.48) is transformed in an equation for \( f_{\text{xc}}(\mathbf{q}, \omega) \):

\[ f_{\text{xc}}(\mathbf{q}, \omega) = \left[ P^0(\mathbf{q}, \omega) \right]^{-1} \delta P(\mathbf{q}, \omega) [P^0(\mathbf{q}, \omega)]^{-1} - \left[ P^0(\mathbf{q}, \omega) \right]^{-1} \delta P(\mathbf{q}, \omega) f_{\text{xc}}(\mathbf{q}, \omega) \]  

(3.52)

Now, expanding \( \delta P(\mathbf{q}, \omega) \) in terms of \( W \) as \( \delta P(\mathbf{q}, \omega) = \sum_n \delta P^{(n)}(\mathbf{q}, \omega) \) from Eq. (3.52) it is possible to write an iterative form for the \( n \)th order contribution \( f^{(n)}_{\text{xc}}(\mathbf{q}, \omega) \) to \( f_{\text{xc}}(\mathbf{q}, \omega) \), i.e.

\[ f^{(n)}_{\text{xc}}(\mathbf{q}, \omega) = \sum_n f^{(n)}_{\text{xc}}(\mathbf{q}, \omega), \text{when all the terms of lower order of the BS are known:} \]

\[ f^{(n)}_{\text{xc}}(\mathbf{q}, \omega) = \left[ P^0(\mathbf{q}, \omega) \right]^{-1} \left[ \delta P^{(n)}(\mathbf{q}, \omega) [P^0(\mathbf{q}, \omega)]^{-1} - \sum_0^{n-1} \delta P^{(m)}(\mathbf{q}, \omega) f^{(n-m)}_{\text{xc}}(\mathbf{q}, \omega) \right] \]  

(3.53)

The first order of such expansion is simply given by:

\[ f^{(1)}_{\text{xc}}(\mathbf{q}, \omega) = \left[ P^0(\mathbf{q}, \omega) \right]^{-1} \delta P^{(1)}(\mathbf{q}, \omega) [P^0(\mathbf{q}, \omega)]^{-1} \]  

(3.54)

where:

\[ \delta P^{(1)}_{G_1, G_2}(\mathbf{q}, \omega) = \sum_{\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3, \mathbf{K}_4} \phi^*_{\mathbf{K}_1}(\mathbf{q}, \mathbf{G}_1) P_{\mathbf{K}_1, \mathbf{K}_2}(\mathbf{q}, \mathbf{G}_1) W_{\mathbf{K}_2, \mathbf{K}_3}(\mathbf{q}) P_{\mathbf{K}_2, \mathbf{K}_3}(\mathbf{q}, \mathbf{G}_2) \phi_{\mathbf{K}_3}(\mathbf{q}, \mathbf{G}_2) \]  

(3.55)

and this is the kernel we have used in chapter 7. Such kernel turns to be non-local in space and frequency dependent. The advantage of the present formalism is that can be consistently improved by going to higher orders. It also allows the calculation of vertex functions and their impact on the lifetimes [Marini 04]. The same formula (3.54) has been independently derived following a different approach by other group [Sottile 03]. It has been proved that such kernel works very well for the calculation of absorption spectra for different systems as LiF, SiO2 and diamond [Marini 03], Si, SiC and Ar [Sottile 03] and Si and GaAs [Adragna 03]. In this works it is also showed the importance of the non-locality and of the frequency dependence of this kernel.
in the various cases, that turns to be crucial in presence of bound excitons. Note that even if Eq. (3.50) is defined with time-ordered Green function, it is possible to define the corresponding causal polarization function. In Ref [Marini 03] the EELS spectrum (that requires causal polarization function) of LiF has been calculated with success, even if a second order in \( f_{xc} \) is needed to have a perfect agreement with the BS result. Until now this TDDFT kernel has been used for bulk systems, and surfaces [Pulci 06], in chapter (7) we will show the performances of such kernel for quasi 1D infinite systems and finite systems. The details of the implementation of this kernel will be described later in section (4.3)
Part II

Numerical and technical developments
4 Numerical implementations

In this section of the thesis we briefly summarize the main features of the implementation of the theory exposed in the first part. In this chapter we provide some details on the codes used to obtain the results exposed in the application part. We focus on the basic points and illustrate the main contributions of the present work. In particular, in the following chapter we describe a new technique that we have developed that permits to handle systems with reduced arbitrary periodicity in supercell techniques. The starting point of our calculations for both in TDDFT and MBPT is the ground state of the system. The ground state in all cases have been calculated in DFT framework either using LDA, GGA or KLI approximations for exchange and correlation effects. Here we stress that it is a first principle method, so no models are applied to approximate the Kohn-Sham Hamiltonian (1.16). The only required approximation are in the choice of the exchange-correlation functional \( v_{xc} \), cfr. section (1.1), and the pseudo-potential method. The latter consists in considering explicitly in the calculation only the chemically active valence electrons. The influence of the core electrons, that are localized close to the nuclei and do not participate in the chemical bonds, is taken into account by an effective "pseudo potential", which reproduces the same eigenvalue and scattering properties of the atom. We work with norm-conserving pseudopotentials, obtained following the prescription of Troullier and Martins [Troullier 91] \(^1\). As seen in section (1) the Kohn-Sham equation are a set of non-linear coupled equations that must be solved self-consistently because the KS Hamiltonian \( \hat{h}_{KS}[n] \) depends on the density that is the sought solution. The ground state of the Kohn Sham N-electron system, will be a Slater determinant solution of Eq. (1.16a) with lower energy (the density will be calculated by Eq. (1.16d)). A general flow chart of the self-consistent Kohn Sham cycle (SCF) is depicted in Fig. 4.1. The starting point is a general approximation of the solution \( \{n^0, \phi^0_i\} \). With this choice of the density (that could be random) the Kohn-Sham Hamiltonian is constructed and then diagonalized using a conjugated gradients method [Payne 92]. From the output wave-functions, a new density is constructed and the

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\(^1\) they can be generated at the OCTOPUS web page: www.tddft.org/programs/octopus.
cycle is repeated until self consistency is achieved. The cycle is stopped when some convergence criterion is satisfied. The most used criteria, are based on the difference of total energies or densities from one iteration and previous one are minor of some tolerance $\eta$, i.e. $|E^{(i)} - E^{(i-1)}| < \eta_E$ or $\int d\mathbf{r} |n^{(i)} - n^{(i-1)}| < \eta_N$. If the convergence criteria it is not satisfied a new density to start a new iteration is constructed, usually mixing the output $n'$ density calculated by Eq. (1.16d) and the densities of previous iterations. The reason for the mixing is due because the use of the output density alone, as input density for a new iteration usually leads to instabilities. There exists different schemes of mixing to avoid instabilities and speed up the convergences [Johnson 88, Bowler 00]. The simplest one consists in construct a linear combination of the density $n'$ and the density of the previous iteration [Dederichs 83]:

$$n^{(i+1)} = \alpha n' + (1 - \alpha) n^i, \quad 0 \leq \alpha \leq 1$$

(4.1)

However in most of the calculations we use the Broyden mixing scheme that is more stable than the simple linear mixing. This is the general scheme for the calculation of the ground state density and KS eigenfunction and eigenvalues. The KS eigenfunction and eigenvalues are the starting point for the calculations of the absorption spectra both in both TDDFT and MBPT (as discussed in section (2.1) and chapter (3)). For these calculations we have employed different basis set for the representation of the orbitals and density: real space and plane wave expansion. The response functions are evaluated in either real time or in frequency domain depending on the property and system under study. In the next we will give a short introduction of these two method and we will discuss the used implementations and approximations.

Figure 4.1: Flow chart of a general Self Consistent Field Cycle for the solution of the KS problem
4.1 Real Space - Real Time representation: the OCTOPUS project

The results reported in sections (6.1) and (6.2) on the optical properties of biological systems have been carried out by means of TDDFT, where the excited states have been calculated by direct evolution of the Time Dependent Kohn-Sham Equation as explained in section (2.2.2). For these calculations we have used the code OCTOPUS. Here we examine some details of the implementation for such calculations and we refer the reader to the paper [Marques 03a], to the Phd thesis of Alberto Castro [Castro 04a] and to the code’s web site for a complete description of the potentiality of this code, as well as for a tutorial and works done with this scheme.

4.1.1 The Grid

In a real space representation, a function $\phi$ is represented by its values set $\phi_j = \phi(r_j)$, where $\{r_j\}$ is a set of points in a given simulation box. We have used an uniform mesh, i.e. the points are equally spaced. The choice of having an uniform grid it is not the most performing discretization, but it turns to be simple and intuitive. However the present implementation allows for adaptive grids that are important for some application where very different localization regions are present in the simulation box. The simulation region can have different shapes, as sphere, cylinder or parallelepiped. For our calculations we tested different shapes and finally we have choose a grid made of overlapping spheres centered around the nuclei with a radius of 4 Å, in this way we get a compromise between computational efficiency and precision in the calculation. The radius of the sphere have to be carefully checked because the wave-functions turns to be sensitive to the boundaries. A great advantage to work with real space grid, besides easiness for parallelization in domains, is that the potential operator is diagonal. To calculate the kinetic term, the Laplacian is discretized and one needs the value of the wave function in the neighboring points:

$$\nabla^2 \phi(r_i) \approx \sum_{j \in K_i} c_j \phi(r_j)$$

(4.2)

where $K_i$ is a set of neighboring point around $r_i$ and $c_j$ are real numbers defined to approximate the Laplacian [Fornberg 94]. The lowest order rule to evaluate the

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3 http://www.tddft.org/programs/octopus
Laplacian operator is in one dimension the three point rule that reads:

\[
\frac{d^2}{dr^2} \phi(r) \bigg|_{r_i} \simeq \frac{1}{4} [\phi(r_{i-1}) - \phi(r_i) + \phi(r_{i+1})]
\]  

(4.3)

In our calculations we have used a higher order 9-point rule that allows to use a larger mesh spacing\(^4\). An important detail is the evaluation of the Hartree term Eq. (1.14). This term is not efficiently evaluated performing a direct integration, and it is obtained solving the Poisson equation:

\[
\nabla^2 v_H(r) = -4\pi n(r)
\]  

(4.4)

This equation is solved in reciprocal space by performing a Fast Fourier Transform. A particular attention have to be paid to completely cancel the spurious cell-cell interaction when Eq. (4.4) is treated in Fourier space (see next chapter). This problem is solved imposing a cutoff to the Coulomb potential, and will be extensively discussed in the next chapter. The parameters that controls the accuracy of the calculation are the mesh spacing \( h \) and the kinetic energy discretization order. Unfortunately we have to mention that the real space implementation as such is not variational, i.e. we can find a total energy lower than the true energy and reducing the grid spacing the total energy can increase. Anyway for practical implementation this is not a problem as the convergence with respect \( h \) can be easily checked.

### 4.1.2 The Time Evolution

In order to calculate the absorption spectra as described in section (2.2.2) the time dependent Kohn-Sham equations (2.2) has to be solved. To propagate the electronic wave-function in real time, we use a scheme designed to enforce time-reversal symmetry as implemented in OCTOPUS, i.e. we assume that the wave-function forward propagated from, \( t \) to \( t + \Delta t / 2 \) must be equal to the function backward propagated from \( t + \Delta t \) to \( t + \Delta t / 2 \), i.e.:

\[
e^{-i\hat{H}(t)\frac{\Delta t}{2}} \phi(t) = e^{i\hat{H}(t+\Delta t)\frac{\Delta t}{2}} \phi(t + \Delta t)
\]  

(4.5)

Such assumption yields:

\[
\phi(t + \Delta t) = e^{-i\hat{H}(t+\Delta t)\frac{\Delta t}{2}} e^{-i\hat{H}(t)\frac{\Delta t}{2}} \phi(t)
\]  

(4.6)

\(^4\) For a general routine to generate the discretization of the kinetic energy operator see the tutorial page of the OCTOPUS code http://www.tddft.org/programs/octopus and ref.[Beck 00, Marques 03a]
4.2 Plane waves

We start by estimating \( \phi(t + \Delta t) \sim e^{-i\hat{H}(t)\Delta t}\phi(t) \) by expanding the exponential to fourth order in \( \Delta t \).

\[
e^{-i\hat{H}\Delta t} \simeq \sum_{n=0}^{4} \frac{(-i\Delta t)^n}{n!} H^n
\]

(4.7)

Then this estimation is used to obtain an approximation for \( \hat{H}(t+\Delta t) \), and finally the expression (4.6) is computed again expanding the exponential to the fourth order.

We used a uniform grid-spacing of 0.23 Å and a time-step of 0.0025 \( h/eV \). These parameters ensure the stability of the time-dependent propagation and yield spectra (Eq. 2.14) with a resolution better than 0.1 eV.

4.2 Plane waves

To calculate electronic properties of solids, a plane-wave expansion of the Kohn-Sham wave functions turns to be very useful, because the periodicity of the system is automatically taken into account working only with primitive cells to calculate bulk properties. In such representation a Bloch wave function in periodic boundary conditions is given by:

\[
\phi_{\mathbf{n}\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{\mathbf{n}\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{n}\mathbf{k}}(\mathbf{r}).
\]

(4.8)

where \( u_{\mathbf{n}\mathbf{k}}(\mathbf{r}) \) is a periodic function. The system is represented in a supercell of volume \( \Omega \), the atoms are placed inside the supercell and translated according to the symmetries properties of the system by the lattice vector \( \mathbf{R}_i \). The vectors \( \mathbf{k} \) lie within the first Brillouin zone (BZ) and \( \mathbf{G} \) are the reciprocal lattice vectors. Other great advantages of using the plane-wave expansion are:

- The translational symmetry of the potentials involved in the calculation is naturally accounted in reciprocal space, and most expressions of the Hamiltonian (1.16b) are analytic. The Kohn-Sham equation (1.16a) in this basis set reads:

\[
\sum_{\mathbf{G}'} \hat{h}_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) c_{\mathbf{n}\mathbf{k}}(\mathbf{G}') = \epsilon_{\mathbf{n}\mathbf{k}} c_{\mathbf{n}\mathbf{k}}(\mathbf{G}),
\]

(4.9)

where the Hamiltonian matrix elements are:

\[
\hat{h}_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) = \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + \nu(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') + \nu_H[n](\mathbf{G} - \mathbf{G}') + \nu_{xc}[n](\mathbf{G} - \mathbf{G}').
\]

(4.10)
In this representation the kinetic term is diagonal, and the Hartree term is easily obtained as:

\[ v_H[n](G) = 4\pi \frac{n(G)}{G^2} \] (4.11)

Note that the external potential depends on both \( G \) and \( G' \) when non-local norm-conserving pseudopotentials are used.

- There exists very efficient algorithms like FFTW\[Frigo 98\] that allow us to calculate the Fourier transform very efficiently. Moreover there exists very efficient pre-conditioning algorithms to speed up the SCF convergence.

- the expansion in plane waves is exact, since they form a complete set, and it is only limited in practice by one parameter, namely, the maximum value of the momentum, that determines the size of the chosen set. The usual criterion to truncate the expansion is given by the convergence of the total energy. This convergence can be achieved increasing the cutoff energy \( E_{\text{cutoff}} \):

\[ \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cutoff}} \] (4.12)

The number of plane wave involved in the calculation \( N_{PW} \) scales as \( N_{PW} \propto \Omega(E_{\text{cutoff}})^{\frac{3}{2}} \).

Although localized basis set are smaller for systems where localized electronic wave functions are involved in the chemical binding, for instance for atoms, molecules and clusters, plane-wave can be also be used in the supercell approach [Cohen 82, Cohen 94, Pickett 89, Payne 92]. In the supercell approximation the physical system is treated as a fully 3D periodic system, but a new unit cell (the supercell) is built in such a way that some extra empty space separates the periodic replica along the directions in which the system is to be considered as finite. This method make possible to retain all the advantages of plane wave expansion mentioned above. However, for finite system, a large number of plane waves is needed because the density in concentrated in a small part of the total volume of the supercell. Moreover the valence wave-functions of the atoms oscillates strongly in the neighbor of the atomic core, due to the orthogonalization to the inner electronic wave function. For this reason the use of pseudopotentials, apart the advantage to manage less electrons, has the further advantage to reduce the energy cutoff. Yet the use of a supercell to simulate objects that are not infinite and periodic in all the directions, leads to artifacts, even if a very large portion of vacuum is interposed between the replica of
the system in the non-periodic dimensions. In fact, the straightforward application of the supercell method generates in any case fake images of the original system, that can mutually interact in several ways, affecting the results of the simulation. This problem is inherent not only to application of plane waves in supercell schemes, but also to other methods where supercell approach is underlying the solution of the many-body electronic problem as quantum-Montecarlo. In order to solve this problem we have developed a cutoff Coulomb potential. The description and the performance of such modified potential is the topic of the next chapter, as well as the convergence problems with respect the empty space needed in the supercell approach for the optical and electronic properties of non 3D systems. In the work exposed in chapter (7), where we have studied optical properties of finite and infinite chains of atoms, we have chosen to work in the supercell approach, and the new cutoff potential has been used in all the calculations. The ground state KS wave-functions and eigenvalues have been calculated using the plane-wave code ABINIT [Gonze 05]. For the optical properties both in TDDFT and MBPT framework we have used the code SELF. This is also a plane wave code, developed in our group, and all the quantities are expressed in reciprocal space, details on how the main quantities have been calculated with this code will be given in the next section.

4.3 Technical details and implementations in the code SELF

The GW calculation

As discussed in section (3.3) in the GW approximation, the non-local energy-dependent electronic self-energy $\Sigma$ plays a role similar to that of the exchange-correlation potential of DFT. $\Sigma$ is approximated by the convolution of the one electron Green’s function and the dynamically screened Coulomb interaction $W$ Eq. (3.21c). The quasiparticle energies have been calculated at the first order of perturbation theory in $\Sigma - V_{xc}$ [Hybertsen 85, Godby 88] as in Eq. (3.24). We first divide the Self-energy in an exchange $\Sigma_x$ and a correlation $\Sigma_c$ parts

$$\langle \phi_j^{DFT} | \Sigma | \phi_i^{DFT} \rangle = \langle \phi_j^{DFT} | \Sigma_x | \phi_i^{DFT} \rangle + \langle \phi_j^{DFT} | \Sigma_c | \phi_i^{DFT} \rangle.$$  (4.13)

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5 http://www.abinit.org
6 http://people.roma2.infn.it/~marini/self
where:

\[
\begin{align*}
\Sigma_x(r, r') &= \imath v(r, r') G^0(r, r', t + 0^-) \\
\Sigma_c(r, r', t) &= \imath \tilde{W}(r, r') G^0(r, r', t)
\end{align*}
\] (4.14a) (4.14b)

Here \(v\) is the bare coulomb potential and \(\tilde{W}\) it is not the full screening but only its frequency dependent part:

\[
\begin{align*}
\tilde{W}(r, r_0; t) &= Z_{d_{r_1}} v(r, r_1) \times \Lambda_{r_0, r_1}(q) G_{0}^0(r, r_0, t) \\
\end{align*}
\] (4.15)

and

\[
\begin{align*}
\Lambda_{r_0, r_1}(q) &= \int d\mathbf{r}_1 v(\mathbf{r}, \mathbf{r}_1) \chi(\mathbf{r}, \mathbf{r}_1, t) \\
\chi(\mathbf{r}, \mathbf{r}_1, t) &= \sum_{n_1, n_2} \int \frac{d^3q}{(2\pi)^3} \sum_{G} v(q + G) \times \rho_{n_1 n_2}(q, G) \rho^*_{n_2 n_1}(q, G) f_{n_1 k_1} (4.16)
\end{align*}
\]

and

\[
\begin{align*}
\langle n|\Sigma_x(r_1, r_2)|n'\rangle &= \frac{1}{2} \sum_{n_1} \int \frac{d^3q}{(2\pi)^3} \sum_{G} v(q + G') \times \rho_{n_1 n_2}(q, G) \rho^*_{n_2 n_1}(q, G') \int \frac{d\omega'}{2\pi} \epsilon_{G'}^{-1}(q, \omega') \\
&\times \left[ \frac{f_{n_1(k-q)}}{\omega - \omega' - \epsilon_{LDA}^{n_1(k-q)} - i\delta} + \frac{1 - f_{n_1(k-q)}}{\omega - \omega' - \epsilon_{LDA}^{n_1(k-q)} + i\delta} \right] \left(4.17\right)
\end{align*}
\]

where \(\rho_{n_1 n_2}(q, G) = \langle n|e^{i(q + G) \cdot r_1}|n_2 k_1\rangle\). The integral in the frequency domain in Eq. (4.17) has been analytically solved considering the dielectric matrix in the plasmon pole model [Godby 89]. This approximation to the inverse dielectric matrix is based on the observation that in realistic calculations of response function \(Im\epsilon^{-1}(\omega)\) is a peaked function in \(\omega\). Such defined peaks corresponds to plasmon excitations of the system. With this in mind we can approximate the energy dependence of the imaginary part of each element of \(\epsilon^{-1}\) with a narrow Lorentzian peak. Using the Kramers-Kroning relation the inverse dielectric matrix in reciprocal space is given by:

\[
\epsilon_{G,G'}^{-1}(\omega) = \delta_{G,G'} + \Omega_{G,G'}/(\omega^2 - \tilde{\omega}_{G,G'}^2) (4.18)
\]

Note that here the energy \(\omega\) is a complex variable. The position \(\tilde{\omega}_{G,G'}\) and the strength \(\Omega_{G,G'}\) of the poles are obtained fitting a full calculation along the imaginary energy axis. So a full calculation for only two frequencies \((\omega = 0\) and \(\omega = iE_0)\)
is needed in order to find the the poles and residuum for each component. We have tested the validity of this approximation performing calculation of the gap either in the case of an infinite polymer of polyacetylene or isolate molecule of $C_2H_4$ (a single monomer of polyacetylene) calculating the $\Sigma_e$ with a direct integration in the frequency domain. Such calculations turns to be very cumbersome and the differences with the results of the gap energy obtained with the plasmon-pole approximation have been less then 5%. Thus, we have decided to use the plasmon-pole approximation for all the calculations presented in chapters (5) and (7).

The Bethe Salpeter equation

We have described in section (3.4) the structure of the Excitonic Hamiltonian, and the different terms of each element of the excitonic matrix have been illustrated in Eqs.(3.44,3.45,3.46). The basis set to describe the exciton state is composed by product states of the occupied and unoccupied LDA single particle states and the coupled electron-hole excited states Eq. (3.41), taking only the resonant term now can be written in terms of electron and hole coordinates as:

$$\Psi_S(\mathbf{r}_h, \mathbf{r}_e) = \sum_{v, c, \mathbf{k}} A_S^{vck}(\mathbf{r}_k^*) \phi_{vck}(\mathbf{r}_h) \phi_{vck}(\mathbf{r}_e)$$

(4.19)

where \{e\} stands for electron and \{h\} for hole. With these assumption, when only the resonant part of the Hamiltonian is taken into account Eq. (3.40) reads:

$$(\epsilon^{QP}_{vck} - \epsilon^{QP}_{vck}) A^{vck}_S + \sum_{vck,v'c'k'} K_{vck,v'c'k'} A^{v'c'k'}_S A^{vck}_S = E_S A^{vck}_S$$

(4.20)

$E_S$ is the excitation energy of the state $\Psi_S$ and $K$ the interaction kernel that includes an unscreened exchange repulsive term $2K^{Exch}$ and a screened electron-hole interaction $K^{dir}$ (direct term). The factor two that multiplies the exchange part enters for considering spin singlet excitations. In plane wave basis such terms for the resonant part read:

$$2K^{Exch, res}_{vck,v'c'k'} = \frac{2}{\Omega} \sum_{G \neq 0} \langle v(G) | e^{i\mathbf{G} \cdot \mathbf{r}} | v(k) \rangle \langle v'k' | e^{-i\mathbf{G} \cdot \mathbf{r}} | v'k' \rangle$$

(4.21)

$$K^{dir, res}_{vck,v'c'k'} = \frac{1}{\Omega} \sum_{G, G'} v(G + q) \epsilon_{GG'}^{-1}(q) \langle v(k) | e^{i(q+G) \cdot \mathbf{r}} | v'k' \rangle \times$$

$$\langle v'k' | e^{-i(q+G) \cdot \mathbf{r}} | v(k) \rangle \delta_{q,k-k'}$$

(4.22)
The screened potential has been treated in static RPA approximation (dynamical effects in the screening have been neglected as it is usually done in present Bethe-Salpeter calculations[Onida 02, Albrecht 98, Benedict 98, Rohlffing 98, Rohlffing 00]). For bulk systems the off-diagonal blocks, of the excitonic matrix (3.43), the so-called coupling terms Eq. (3.46) are found to be small and have nearly no effect on the excitation energies [Albrecht 98, Rohlffing 98]. However, as we will see in chapter (7), for finite systems they can play a role. For this reason we have implemented the coupling terms in the code SELF. The unscreened exchange term is from Eq. (3.46):

\[ 2K^{\text{Exch,cpl}}_{c,c'} = \frac{2}{\Omega} \sum_{G \neq 0} v(G) \langle ck | e^{iG \cdot r} | vk \rangle \langle c'k' | e^{-iG' \cdot r} | v'k' \rangle \]  

(4.23)

and the direct screened coulomb term:

\[ K^{\text{dir,cpl}}_{c,c'} = \frac{1}{\Omega} \sum_{G,G'} v(q+G) e^{-G \cdot G'} \langle ck | e^{i(G+q) \cdot r} | v'k' \rangle \times \langle c'k' | e^{-i(G+q) \cdot r} | vk \rangle \delta_{q,k-k'} \]  

(4.24)

Note that when the coupling terms are taken into account, the dimension of excitonic matrix to diagonalize is four times bigger than the only-resonant case, with the additional complication that the matrix is no more Hermitian.

The \( f_{xc} \) kernel from the Bethe Salpeter equation

In section (3.5) we have derived an expression for a non-local and energy dependent kernel imposing that TDDFT reproduce the perturbative expansion of the BS equation in terms of the screened coulomb potential. At first order the expression of \( f_{xc} \) is given in Eq. (3.54). A direct application of this expression leads to spurious oscillations, and in many case it give rise to non-physical regions of negative absorption. The reason of such oscillations is imputable to the diagonal part of the kernel of the BS equation (Eq. 3.51). The diagonal part of the BS equation:

\[ \Delta^{(q)}_{K} = W_{K,K}(q) \]  

(4.25)

is responsible for the shifting of the spectra, and can be shown [Marini 03] that it appears in \( f_{xc} \) through a series expansion in \( \Delta^{(q)}_{K} \). Of course, a perturbative treatment is meaningful only if \( \Delta^{(q)}_{K} \) is small. This is not the case for the systems that we have treated in chapter (7), where it is of the order of 1 eV. To overcome this
issue we include the diagonal part of the kernel of the BS equation in the independent quasiparticle response function $P^0(q, \omega)$, and the $f_{xc}$ will take into account all the off-diagonal contribution. Explicitly we can rewrite the equation (3.50) as:

$$P^{BS}_{k_1,k_2}(q, \omega) = P^0_{k_1,k_2}(q, \omega + \Delta) - P^0_{k_1,k_3}(q, \omega + \Delta) \tilde{W}_{k_3,k_4}(q) P^{BS}_{k_4,k_2}(q, \omega)$$

(4.26)

where now

$$\tilde{W}_{k_1,k_2} = \begin{cases} 0 & K_1 = K_2 \\ W_{k_1,k_2} & \text{otherwise} \end{cases}$$

(4.27)

and the corresponding expression for the $f_{xc}^{(1)}$ will be now given by:

$$f_{xc}^{(1)}(q, \omega) = [P^0(q, \omega + \Delta)]^{-1}\delta P^{(1)}(q, \omega)[P^0(q, \omega + \Delta)]^{-1}$$

(4.28)

where in the expression of $\delta P^{(1)}$ (Eq. (3.55)) the diagonal part of $W$ has been removed. With this trick the TDDFT calculations of the absorption spectra are numerically stable. Moreover we have applied a fast procedure to calculate the kernel at first order as indicated in Ref. [Marini 03]. Looking ad the analytic properties of $\delta P^{(1)}$ Eq. (3.55), the contribution of degenerate non-interacting electron-hole states in Eq. (3.34) are singled out and the expression for $f_{xc}$ reads:

$$f_{xc}^{(1)}(q, \omega) = \frac{2}{\Omega} [P^0(q, \omega + \Delta)]^{-1} \sum_{k} \left[ \frac{R_{k}^{(q)} + R_{k}^{(q)^\dagger}}{\omega + \Delta_{k}^{(q)} - E_{k}^{(q)} + i\eta} + \frac{Q_{k}^{(q)}}{(\omega + \Delta_{k}^{(q)} - E_{k}^{(q)} + i\eta)^2} \right]$$

$$\times [P^0(q, \omega + \Delta)]^{-1}$$

(4.29)

Here the sum runs over the independent electron-hole states and the residuum are given by:

$$[R_{k}^{(q)}]_{G_1,G_2} = \sum_{k',\epsilon_{k'}^{(q)} \neq \epsilon_{k}^{(q)}} \frac{\Phi^{*}K(q, G_1)W_{k,k'}(q)\Phi K'(q, G_2)}{E_{k}^{(q)} - E_{k'}^{(q)}}$$

for non degenerate states

$$[Q_{k}^{(q)}]_{G_1,G_2} = \sum_{k',\epsilon_{k'}^{(q)} = \epsilon_{k}^{(q)}} \frac{\Phi^{*}K(q, G_1)W_{k,k'}(q)\Phi K'(q, G_2)}{E_{k'}^{(q)} - E_{k}^{(q)}}$$

for degenerate states

(4.30)

Eq. (4.29) turns to be much faster to calculate than Eq. (3.55): it has the form of a non-interacting polarization function with modified residuals that are evaluated only once by a two matrix-vector multiplication. Looking at the expression
(4.28) to obtain the many-body based $f_{xc}$ we can see that another complication arise. Until now we have implicitly assumed that $P^0$ is an invertible matrix. Mearns and Kohn [Mearns 87] showed that when the energy range taken into account is above the first resonance, as in the case of the absorption spectra, non trivial vanishing eigenvalue occurs, and the inversion leads to numerical problems. We have overcome this problem using the Singular Value Decomposition (SVD) [Press 92], finding a window for the threshold that give stable solution for the spectra shown in chapter (7).
5 An exact Coulomb cutoff technique for supercell calculations

In section (4.2) we have described the main advantages of the use of plane-wave basis set in the calculation of electronic and optical properties of infinite crystal solids. However, mainly in the last decade, increasing interest has been developed in systems at the nano-scale, like tubes, wires, quantum-dots, biomolecules, etc., whose physical dimensionality is, for all practical purposes, less than three [Nalwa 05]. These systems are still 3-dimensional (3D), but their quantum properties are those of a confined system in one or more directions, and those of a periodic extended system in the remaining directions. Other classes of systems with the same kind of reduced periodicity are the classes of the polymers, and of the solids with defects. Throughout this chapter we call nD-periodic a 3D object, that can be considered infinite and periodic in \( n \) dimensions, being finite in the remaining \( 3 - n \) dimensions. It is well known that the response function of an overall neutral solid of molecules is not equal, in general, to the response of the isolated molecule, and converges very slowly to it, when the amount of vacuum in the supercell is progressively increased [Onida 02, Sottile 05]. For instance, the presence of higher order multipoles can make undesired images interact via the long range part of the Coulomb potential. In the dynamic regime, multipoles are always generated by the oscillations of the charge density even in systems whose unit cell does not carry any multipole in its ground state. This is the case, for example, when we investigate the response of a system in presence of an external oscillating electric field. Things go worse when the unit cell carries a net charge, since the total charge of the infinite system represented by the supercell is actually infinite, while the charges at the surfaces of

\[\text{This section is largely an adaptation of the article: C.A. Rozzi, D. Varsano, A. Marini, A. Rubio and E.K.U. Gross: An exact Coulomb cutoff technique for supercell calculations accepted in Phys. Rev. B (2006). As such, the reported work includes collaboration of the rest of the authors of the article. The paper can be download from cond-mat 0601031} \]
a finite, though very large, system always generate a finite polarization field. This situation is usually normalized in the calculation by the introduction of a suitable compensative positive background charge. Another common situation in which the electrostatics is known to modify the ground state properties of the system occurs when a layered system is studied, and an infinite array of planes is considered instead of a single slab, being in fact equivalent to an effective chain of capacitors [Wood 04]. These issues become particularly evident in all the approaches that imply the calculation of non-local operators or response functions, because, in these cases, two supercells may effectively interact even if their charge densities do not overlap at all. This is the case, for example, of the many-body perturbation theory calculations (MBPT), and, in particular, of the self-energy calculations at the GW level. However we are usually still interested in the dispersion relations of the elementary excitations of the system along its periodic directions, and those are ideally dealt with using a plane waves approach. Therefore, the ideal path to keep the advantages of the supercell formulation in plane waves on the use of FFT to solve the Poisson equation, even in real space implementation, and to gain a description of systems with reduced periodicity free of spurious effects is to develop a technique to cut the Coulomb interaction off out of a desired region. FFT turns to be very fast and this approach is worth compared to other multipole expansion that allow to treat the proper boundary conditions for the Poisson equation in real space without resorting to supercell approach. This problem is not new and has been addressed now for a very long time and in different fields and several different approaches have been proposed in the past to solve it. The aim of the present work is to focus on the widely used supercell schemes to show how the image interaction influences both the electronic ground state properties and the dynamical screening in the excited state of 0D-, 1D-, 2D-periodic systems, and to propose an exact method to avoid the undesired interaction of the replicas in the non-periodic directions. The chapter is organized as follows: in section (5.1) we review more in detail the problem of the solution of the Poisson equation in the plane wave method for solids, in section (5.2) the new method is outlined, in section (5.3) the treatment of the singularities is explained, in section (5.4) some applications of the proposed technique are discussed.
5.1 The 3D-periodic case

The main problem of electrostatics we are facing here can be reduced to the problem of finding solutions to the Poisson equation for a given charge distribution $n(r)$, and given boundary conditions

$$\nabla^2 V(r) = -4\pi n(r).$$

(5.1)

In a finite system the potential is usually required to be zero at infinity. In a periodic system this condition is meaningless, since the system itself extends to infinity. Nevertheless the general solution of Eq. (5.1) in both cases is known in the form of the convolution

$$V(r) = \iiint_{\text{space}} \frac{n(r')}{|r-r'|} d^3 r',$$

(5.2)

that it is referred from now on as the Hartree potential. It might seem that the most immediate way to build the solution potential for a given charge distribution is to compute the integral in real space, but problems immediately arise for infinite systems. In fact, the density can be reduced to an infinite sum over delta charge distributions $q\delta(r-r')$, and the integral in Eq. (5.2) becomes an infinite sum as well, but this sum is in general only conditionally, and not absolutely convergent.[Makov 95]

$$V(r) = \sum_n \frac{q}{|r-L_n|},$$

(5.3)

This sum gives a potential that is determined up to a constant for a neutral cell with zero dipole moment, while the corresponding sum for the electric field is absolutely convergent. A neutral cell with a non null dipole moment, on the opposite, gives a divergent potential, and an electric field that is determined up to an unknown constant electric field (the sum for the electric field is conditionally convergent in this case). Even if, in principle, the surface terms have to be always taken into account, in practice they are only relevant when we want to calculate energy differences between states with different total charge. These terms can be neglected in the case of a neutral cell whose lowest nonzero multipole is quadrupole[DeLeeuw 80].

As in the present work we are interested in macroscopic properties of the periodic system, those surface effects are never considered in the discussion that follows. However this sample-shape effects play an important role for the analysis of different spectroscopies as, for example, infrared and nuclear-magnetic resonance. A major source of computational problems is the fact that the sum in Eq. (5.3) is very slowly converging when it is summed in real space, and this fact has historically
motivated the need for reciprocal space methods to calculate it. It was Ewald who first discovered that, by means of an integral transform, the sum can be split in two terms, and that if one is summed in real, while the other in reciprocal space, both of them are rapidly converging.\cite{Ewald21} The point of splitting is determined by an arbitrary parameter. Let us now focus on methods of calculating the sum in Eq. (5.3) purely based on the reciprocal space. If we consider a periodic distribution of charges with density $n(r)$ such that $n(r) = n(r + L_n)$, with $L_n = \{n_xL_x, n_yL_y, n_zL_z\}$, and \{\textit{n}_x, \textit{n}_y, \textit{n}_z\} $\in \mathbb{Z}$, it turns out that the reciprocal space expression for a potential like

$$V(r) = \iiint_{\text{space}} n(r')v(|r - r'|)d^3r', \quad (5.4)$$

in a 3D-periodic system, can be written as

$$V(G_n) = n(G_n)v(G_n), \quad (5.5)$$

where we have used the convolution theorem to transform the real space convolution of the density and the Coulomb potential into the product of their reciprocal space counterparts. Here $G_n = \{n_xG_x, n_yG_y, n_zG_z\}$ are the multiples of the primitive reciprocal space vectors $\frac{2\pi}{L_n}$, and $v(G_n)$ is the Fourier transform of the long range interaction $v(r)$, evaluated at the point $G_n$. For the Coulomb potential it is

$$v(G_n) = \frac{4\pi}{G_n^2}. \quad (5.6)$$

Fourier transforming expression (5.5) back into real space we have, for a unit cell of volume $\Omega$,

$$V(r) = \frac{4\pi}{\Omega} \sum_{n \neq 0} \frac{n(G_n)}{G_n^2} \exp(iG_n \cdot r). \quad (5.7)$$

At the singular point $G_x = G_y = G_z = 0$ the potential $V$ is undefined, but, since the value at $G = 0$ corresponds to the average value of $V$ in real space, it can be chosen to be any number, corresponding to the arbitrariness in the choice of the static gauge (a constant) for the potential. Observe that the same expression can be adopted in the case of a charged unit cell, but this time, the arbitrary choice of $v(G)$ in $G = 0$ corresponds to the use of a uniform background neutralizing charge.

### 5.2 System with reduced periodicity

It has been shown\cite{Spohr94} that the slab capacitance effect mentioned in the introduction actually is a problem that cannot be solved by just adding more vac-
uum to the supercell. This has initially led to the development of corrections to Ewald's original method [Yeh 99], and then to rigorous extensions in 2D and 1D [Martyna 99, Brodka 03]. The basic idea is to restrict the sum in reciprocal space to the reciprocal vectors that actually correspond to the periodic directions of the system. These approach are in general of order $O(N^2)$ [Heyes 77, Grzybowski 00], but they have been recently refined to order $O(N \ln N)$ [Mináry 02, Mináry 04].

Another class of techniques, developed so far for finite systems, is based on the expansion of the interaction into a series of multipoles (fast multipole method) [Greengard 88, Castro 03, Kudin 04]. With this technique it is possible to evaluate effective boundary conditions for the Poisson’s equations at the cell’s boundary, so that the use of a supercell is not required at all, making it computationally very efficient for finite [Greengard 88, Castro 03] and extended systems [Kudin 04].

Differently from what happens for the Ewald sum, the method that we propose to evaluate the sum in Eq. (5.3), entirely relies on the Fourier space and amounts to screening the unit cell from the undesired effect of (some of) its periodic images. The basic expression is Eq. (5.5), whose accuracy is only limited by the maximum value $G_N$ of the reciprocal space vectors in the sum. Since there is no splitting between real and reciprocal space, no convergence parameters are required. Our goal is to transform the 3D-periodic Fourier representation of the Hartree potential of Eq. (5.5) into the modified one

$$\tilde{V}(G_n) = \tilde{n}(G_n)\tilde{v}(G_n)$$

such that all the interactions among the undesired periodic replica of the system disappear. The present method is a generalization of the method proposed by Jarvis et al. [Jarvis 97] for the case of a finite system. In order to build this representation, we want to:

i. define a screening region $D$ around each charge in the system, out of which there is no Coulomb interaction

ii. calculate the Fourier transform of the desired effective interaction $\tilde{v}(r)$ that equals the Coulomb potential in $D$, and is 0 outside $D$:

$$\tilde{V}(r) = \begin{cases} \frac{1}{r} & \text{if } r \in D \\ 0 & \text{if } r \notin D \end{cases}$$

iii. Finally we must modify the density $n(r)$ in such a way that the effective density is still 3D-periodic, so that the convolution theorem can be still applied,
but densities belonging to undesired images are not close enough to interact through \( \tilde{v}(r) \).

The choice of the region \( D \) for step i) is suggested by symmetry considerations, and it is a sphere (or radius \( R \)) for finite systems, an infinite cylinder (of radius \( R \)) for 1D-periodic systems, and an infinite slab (of thickness \( 2R \)) for 2D-periodic systems. Step ii) means that we have to calculate the modified Fourier integral

\[
\tilde{V}(G) = \iiint_{\text{space}} \tilde{v}(r)e^{-iG \cdot r} d^3r = \iiint_{D} v(r)e^{-iG \cdot r} d^3r.
\]  

(5.10)

Still we have to avoid that two neighboring images interact by taking them far away enough from each other. Then step iii) means that we have to build a suitable supercell, and re-define the density in it. Let us examine first step ii), i.e. the cutoff Coulomb interaction in reciprocal space. We know the expression of the potential when it is cutoff in a sphere.[Jarvis 97] It is

\[
\tilde{v}^{0D}(G) = \frac{4\pi}{G^2} \left[ 1 - \cos(GR) \right].
\]

(5.11)

The limit \( R \to \infty \) converges in a oscillatory form to the bare Coulomb term in the sense of a distribution, while, since \( \lim_{G \to 0} = 2\pi R^2 \), there is no particular difficulty in the origin. This scheme has been successfully used in many applications[Makov 95, Jarvis 97, Castro 03, Marques 03a, Onida 95]. The 1D-periodic case applies to systems with infinite extent in the \( x \) direction, and finite in the \( y \) and \( z \) directions. The effective Coulomb interaction is then defined in real space to be 0 out of a cylinder of radius \( R \) having its axis parallel to the \( x \) direction. By performing the Fourier transformation we get the following exact expression for the cutoff coulomb potential in cylindrical coordinates:[I.S. Gradshteyn 80]

\[
\tilde{v}^{1D}(G_x, G_\perp) = \frac{4\pi}{G_x} \left[ 1 + G_\perp R J_1(G_\perp R)K_0(|G_x|R) - |G_x|RJ_0(G_\perp R)K_1(|G_x|R) \right],
\]

(5.12)

where \( J \) and \( K \) are the ordinary and modified cylindrical Bessel functions, and \( G_\perp = \sqrt{G_y^2 + G_z^2} \). It is easy to realize that, since the \( K \) functions damp the oscillations of the \( J \) functions very quickly, for all practical purposes this cutoff function only acts on the very first smaller values of \( G \), while the unscreened \( \frac{4\pi}{G^2} \) behavior is almost unchanged for the larger values. Unfortunately, while the \( J_n(\xi) \) functions have a constant value for \( \xi = 0 \), and the whole cutoff is well defined for \( G_\perp = 0 \), the \( K_0(\xi) \)
5.2 System with reduced periodicity

function diverges logarithmically for \( \xi \to 0 \). Since, on the other hand, \( K_1(\xi) \approx \xi^{-1} \) for small \( \xi \),

\[
\tilde{V}^{1D}(G_x, G_\perp) \sim -\log(G_x R) \quad \text{for } G_\perp > 0, G_x \to 0^+. \tag{5.13}
\]

This means that the limit \( \lim_{G \to 0^+} v(G) \) does not exist for this cutoff function, and the whole \( G_x = 0 \) plane is ill-defined. We will come back to the treatment of the singularities in the next section. We notice that this logarithmic divergence is the common dependence one would get for the electrostatic potential of a uniformed charged 1D wire\cite{Jackson 75}, it is expected that bringing charge neutrality in place would cancel this divergence (see below). The 2D-periodic case, with finite extent in the \( z \) direction, is calculated in a similar manner. The effective Coulomb interaction is defined in real space to be 0 out of a slab of thickness \( 2R \) symmetric with respect to the \( xy \) plane. In Cartesian coordinates we get

\[
\tilde{v}^{2D}(G_\parallel, G_z) = \frac{4\pi}{G^2} \left[ 1 + e^{-G_\parallel R} \frac{|G_z|}{G_\parallel} \sin(|G_z|R) - e^{-G_\parallel R} \cos(|G_z|R) \right], \tag{5.14}
\]

where \( G_\parallel = \sqrt{G_x^2 + G_y^2} \). In the limit \( R \to \infty \) the unscreened potential \( \frac{4\pi}{G^2} \) is recovered. Similarly to the case of 1D, the limit \( G \to 0 \) does not exist, since for \( G_z = 0 \), the cutoff has a finite value, while it diverges in the limit \( G_\parallel \to 0 \)

\[
\tilde{V}^{2D}(G_\parallel, G_z) \sim \frac{1}{G_\parallel^2} \quad \text{for } G_\parallel > 0, G_z \to 0^+. \tag{5.15}
\]

So far we haven’t committed to a precise value of the cutoff length \( R \). This value has to be chosen, for each dimensionality, in such a way that it avoids the interaction of any two neighbor images of the unit cell in the non-periodic dimension. In order to fix the values of \( R \) we must choose the size of the supercell. This leads us to the step 3) of our procedure. We recall that even once the long range interaction is cutoff out of some region around each component of the system, this is not sufficient yet to avoid the interaction among undesired images. The charge density has to be modified, or, equivalently, the supercell has to be built in such a way that two neighboring densities along every non periodic direction do not interact via the cutoff interaction. It is easy to see how this could happen in the simple case of a 2D square cell of length \( L \): if both \( \mathbf{r} \) and \( \mathbf{r}' \) belongs to the cell, then \( r, r' \leq L \), and \( |\mathbf{r} - \mathbf{r}'| \leq \sqrt{2}L \) (see the schematic drawing in Fig. 5.1). If a supercell is built that is smaller than \( (1 + \sqrt{2})L \), there could be residual interaction, and the cutoff would no longer lead to the exact removal of the undesired interactions. Let us call \( A_0 \) the
Figure 5.1: Schematic description for the supercell construction in a 2D system. The upper scheme corresponds to the 2D-periodic case (i.e. a 2D crystal). The middle sketch corresponds to a 0D-periodic system, and the bottom one to a 1D-periodic. In the 0D-periodic case the system in different cells do not interact while in the 1D-periodic the chains do not interact, but within each chain the interaction of all of its elements is permitted.

unit cell of the system we are working on, and $\mathcal{A} = \{A_i, i = -\infty, \cdots, \infty\}$ the set of all the cells in the system. If the system is nD-periodic this set only includes the periodic images of $A_0$ in the $n$ periodic directions. Let us call $\mathcal{B}$ the set of all the non-physical images of the system, i.e. those in the non-periodic directions. Then $\mathcal{A} \cup \mathcal{B} = \mathbb{R}^3$. Obviously, if the system is 3D-periodic $\mathcal{A} = \mathbb{R}^3$, and $\mathcal{B} \equiv \emptyset$. In general we want to allow the interaction of the electrons in $A_0$ with the electrons in all the cells $A_i \in \mathcal{A}$, but not with those $B_i \in \mathcal{B}$. To obtain this we define the supercell
\[ C_0 \supseteq A_0 \text{ such that, } \forall i \]
\[
\begin{cases} 
\text{if } \mathbf{r} \in A_0, \text{ and } \mathbf{r}' \in A_i & \text{then } |\mathbf{r} - \mathbf{r}'| \in C_0 \\
\text{if } \mathbf{r} \in A_0, \text{ and } \mathbf{r}' \in B_i & \text{then } |\mathbf{r} - \mathbf{r}'| \notin C_0 
\end{cases}
\] (5.16)

(see Fig. 5.1 for a simplified 2D sketch). The new density \( \tilde{n}(\mathbf{r}) \) is such that
\[
\begin{cases} 
\text{if } \mathbf{r} \in A_0 & \text{then } \tilde{n}(\mathbf{r}) = n(\mathbf{r}), \\
\text{if } \mathbf{r} \in C_0, \text{ and } \mathbf{r} \notin A_0 & \text{then } \tilde{n}(\mathbf{r}) = 0.
\end{cases}
\] (5.17)

The size of the super-cell in the non-periodic directions depends on the periodic dimensionality of the system. In order to completely avoid any interaction, even in the case the density of the system is not zero at the cell border, it has to be
\[
\begin{align*}
L_C &= (1 + \sqrt{3}) L_A \quad \text{for finite} \\
L_C &= (1 + \sqrt{2}) L_A \quad \text{for 1D-periodic} \\
L_C &= 2 L_A \quad \text{for 2D-periodic}
\end{align*}
\] (5.18)

Actually, since the required super-cell is quite large, a compromise between speed and accuracy can be achieved in the computation, using parallelepiped super-cell with \( L_C = 2L_A \) for all the cases. This approximation rests on the fact that, usually, the charge density is contained in a region smaller than the cell in the non-periodic directions, so that the spurious interactions are, in fact, avoided, even with a smaller cell. Therefore, on the basis of this approximation, we can choose the value of the cutoff length \( R \) always as half the smallest primitive vector in the non-periodic dimension.

## 5.3 Cancellation of singularities

The main point in the procedure of eliminating the divergences in all the cases of interest is to observe that our final goal is usually not to obtain the expression of the Hartree potential \( \textit{alone} \), because all the physical quantities depend on the total potential, i.e. on the sum of the electronic and the ionic potential. When this sum is considered we can exploit the fact that each potential is defined up to an arbitrary additive constant, and choose the constants consistently for the two potentials. Since we know in advance that the sum must be finite, we can include into this constants all the infinities, provided we find a method to separate them.
out of the long range part of both potentials on the same footing. In what follows we show how charge neutrality can be exploited to obtain the exact cancellations when operating with the cutoff expression of section (5.2) in Fourier space. The total potential of the system is built in the following way: we separate out first short and long range contributions to the ionic potential by adding and subtracting a Gaussian charge density $n_+(r) = Z \exp(-a^2 r^2)$. The potential generated by this density is $V_+(r) = Z \frac{\text{erf}(ar)}{r}$. The ionic potential is then written as

$$V(r) = \Delta V(r) - Z \frac{\text{erf}(ar)}{r}, \quad (5.19)$$

where $a$ is chosen so that $\Delta V(r)$ is localized within a sphere of radius $r_a$, smaller than the cell size. The expression of the ionic potential in reciprocal space is

$$V(G) = 4\pi \left[ \int_{0}^{+\infty} \frac{r \sin(Gr)}{G} \Delta V(r) dr - \frac{\exp\left(-\frac{G^2}{4a^2}\right)}{G^2} \right] \quad (5.20)$$

which, for $G = 0$ gives a finite contribution from the first term, and a divergent contribution from the second term

$$V(G = 0) = 4\pi \int_{0}^{+\infty} r^2 \Delta V(r) dr - \infty. \quad (5.21)$$

The first is the contribution of the localized charge, and is easily computed, since the integrand is zero for $r > r_a$. The second term is canceled by the corresponding $G = 0$ term in the electronic Hartree potential, due to the charge neutrality of the system. This trivially solves the problem of the divergences in 3D-periodic systems. Now let us consider a 1D-periodic system. The Hartree term alone in real space is given by

$$V(x, y, z) = \sum_{G_x} \iint_{\Omega} n(G_x, y', z') v(G_x, y - y', z - z') e^{iG_xx'} dy' dz'. \quad (5.22)$$

Invoking the charge neutrality along the chain axis, we have that the difference between electron and ionic densities satisfies

$$\int \int [n_{\text{ion}}(G_x = 0, y, z) - n_{\text{el}}(G_x = 0, y, z)] dy dz = 0. \quad (5.23)$$

Unfortunately, the cutoff function in Eq. (5.12) is divergent for $G_x = 0$. So the effective potential results in an undetermined $0 \cdot \infty$ form. However, we can work
out an analytical expression for it based on conditional convergence of the Coulomb potential in periodic system, by defining a finite cylindrical cutoff and then making the limit of the size of the cylinder to infinity. In this way, as first step, we get a new cutoff interaction in a finite cylinder of radius \( R \), and length \( h \), assuming that \( h \) is much larger than the cell size in the periodic direction. In this case the modified finite cutoff potential includes a term:

\[
\tilde{V}^{1D}(G_x = 0, r) \propto \log\left(\frac{h + \sqrt{h^2 + r^2}}{r}\right) \tag{5.24}
\]

which, in turn, gives, for the particular plane \( G_x = 0 \),

\[
\tilde{v}^{1D}(G_x = 0, G_\perp) \approx -4\pi \int_0^R r J_0(G_\perp r) \log(r) dr + 4\pi R \log(2h) \frac{J_1(G_\perp R)}{G_\perp}. \tag{5.25}
\]

The effective potential is now split into two terms, but only the second one depends on \( h \). The second step is achieved by going to the limit \( h \to +\infty \), to obtain the exact infinite cutoff. By calculating this limit, we notice that only the second term in Eq. (5.25) diverges. This term is the one that can be dropped due to charge neutrality (in fact it has the same form for the ionic and electronic charge densities). Thus, for the cancellation to be effective in a practical implementation we have to treat on the same way both the ionic and Hartree Coulomb contributions. Of course the first term has always to be taken into account, affecting both the long and the short range part of the cutoff potentials. Following this procedure, we are able to get a considerable computational advantage, compared to the method originally proposed by Spataru et al [Spataru 04a], since our cutoff is just an analytical function of the reciprocal space coordinates, and the evaluation of an integral for every value of \( G_x, G_\perp \) is not needed. The cutoff proposed in Ref.[Spataru 04a] is actually a particular case of our cutoff, obtained by using the finite cylinder for all the components of the \( G \) vectors: in this case the quadrature in Eq. (5.25) has to be evaluated for each \( G_x, G_y \) and \( G_z \), and a convergence study in \( h \) is mandatory. In the 1D-periodic case, the \( G = 0 \) value is now well defined, and it turns out to be

\[
\lim_{G_\perp \to 0} \tilde{v}(G_x, G_\perp) = -\pi R^2 (2\log(R) - 1). \tag{5.26}
\]

The analogous result for the 2D-periodic cutoff is obtained by imposing finite cutoff sizes \( h_x = \alpha h_y = h \) (much larger than the cell size), in the periodic directions \( x \) and
Chapter 5. An exact Coulomb cutoff technique for supercell calculations

Figure 5.2: Shape of the cutoff potential \((R_c = 9 \text{a.u.})\). **Left:** In reciprocal space for the \(G_\perp = 0\) (right) and \((q + G)_x = 0\) components. **Right:** Cutoff cylindrical coulomb potential in R-space in the spatial directions parallel and perpendicular to the chain. The unit cell size is \(4.643 \times 33 \times 33 \text{a.u.}\). The R-space shape has been obtained performing back Fourier transform of the expression (5.12) calculated for 21,000 \(\mathbf{G}\) vectors and 61 \(\mathbf{K}\) point in the axial direction and it is compared with the simple analytical form of Eq. (5.9).

\(y\), and dropping the \(h\) dependent part before passing to the limit \(h \to +\infty\). The constant \(\alpha\) is the ratio \(L_x/L_y\) between the in plane lattice vectors.

\[
\tilde{v}^{2D}(G_\parallel = 0, G_z) \approx \frac{4\pi}{G_z^2} [1 - \cos(G_zR) - G_zR \sin(G_zR)]
+ 8h \log \left( \frac{(\alpha + \sqrt{1 + \alpha^2})(1 + \sqrt{1 + \alpha^2})}{\alpha} \right) \frac{\sin(G_zR)}{G_z}. \tag{5.27}
\]

The \(G = 0\) value is

\[
\tilde{v}^{2D}(G_\parallel = 0, G_z = 0) = -2\pi R^2 \tag{5.28}
\]

To summarize, the divergences can be canceled also in 1D-periodic and 2D-periodic systems provided that 1) we apply the cutoff function to both the ionic and the electronic potentials, 2) we separate out the infinite contribution as shown above, and 3) we properly account for the short range contributions as stated in Table 5.1. The analytical results of the present work are condensed in Tab. 5.1: all the possible values for the cutoff functions are listed there as a quick reference for the reader. In Fig. 5.2 we show the the shape of the cylindrical cutoff in G-space for the component \(G_x = 0\) and \(G_\perp = 0\) and its Fourier Transform in R-space compared to the analytical form of Eq. (5.9).
Table 5.1: Reference Table summarizing the results of the cutoff work for all cases: finite systems (0D), one-dimensional systems (1D) and two-dimensional systems (2D). The complete reciprocal space expression of the Hartree potential is provided. For the 1D case, $R$ stands for the radius of the cylindrical cutoff whereas in the 0D case is the radius of the spherical cutoff. In 2D stands for half the thickness of the slab cutoff.

5.4 Results

The scheme illustrated above has been implemented both in the real space time-dependent DFT code OCTOPUS, and in the plane wave many-body-perturbation-theory (MBPT) code SELF. The tests have been performed on the prototypical cases of infinite chains of atoms along the $x$ axis. The comparisons are performed between the 3D-periodic calculation (physically corresponding to a crystal of chains), and the 1D-periodic case (corresponding to the isolated chain) both in the usual supercell approach, and within our exact screening method. We addressed different properties to see the impact of the cutoff at each level of calculation, from the ground state to excited state and quasiparticle dynamics.
5.4.1 Ground state calculations

All the ground state calculations have been done with the real-space implementation of DFT in the OCTOPUS code. We have used non-local norm-conserving pseudopotentials [Troullier 91] to describe the electron-ion interaction and the local-density approximation (LDA) [Perdew 81] to describe exchange-correlation effects. The particular choice of exchange-correlation or ionic-pseudopotential does not matter here as we want to assert the impact of the Coulomb cutoff and this is independent of those quantities. Moreover, we have used a grid of 0.38 a.u. for Si and Na. In this case the footprint of the interaction of neighboring chains in the $y$ and $z$ direction is the dispersion of the bands in the corresponding direction of the Brillouin zone. However it is known that, if the supercell is large enough, the bands along the $\Gamma - X$ direction are unchanged. This is in apparent contradiction with the fact that the radial ionic potential for a wire (that asymptotically goes like ln($r$) as a function of the distance $r$ from the axis of the wire) is completely different from the crystal potential. The answer to this contradiction is clear if we perform a cutoff calculation. In fact the overall effect on the occupied states turns out to be canceled by the Hartree potential, i.e. by the electron screening of the ionic potential, but two different scenarios are visible as soon as the proper cutoff is used. In the top panel of Fig. 5.3 it is shown the ionic potential, the Hartree potential, and their sum for a Si atom in a parallelepiped supercell with side lengths of 2.5, 11, and 11 a.u. respectively in the $x$, $y$ and $z$ directions. No cutoff is used here. The ionic potential is roughly behaving like $\frac{1}{r}$ in the area not too close to the nucleus (where the pseudopotential takes over). The total potential, on the other hand, falls off rapidly to an almost constant value at around 4 a.u. from the nuclear position, by effect of the electron screening. The bottom panel of Fig. 5.3 shows the results when the cutoff is applied (the radius of the cylinder is $R = 5.5$ a.u. such that there is zero interaction between cells). The ionic potential now behaves like it is expected for a potential of a chain, i.e. diverges logarithmically, and is clearly different from the latter case. Nevertheless the sum of the ionic and Hartree potential is basically the same as for the 3D-periodic system. In the static case the two band structure are then expected, and are found to be the same, confirming that, as far as static calculation are performed, the supercell approximation is good, provided that the supercell is large enough (see left part of Fig. 5.4). In static calculations, then, the use of our cutoff only has the effect of allowing us to eventually use a smaller supercell, what provides clear computational savings. In the case of the Si-chain a
Figure 5.3: Calculated total, ionic and Hartree potentials for a 3D-periodic (top) and 1D-periodic (bottom) Si chain.

full 3D calculation would need of a cell size of 38 a.u. whereas the cutoff calculation would give the same result with a cell size of 19 a.u. Of course, when more delocalized states are considered, like higher energy unoccupied states, larger differences
Figure 5.4: Left: Band structure of Si linear chain in a supercell size of 4.9x19x19 a.u. Right: Effect of the cutoff in the band structure of a Na linear chain in a supercell size of 7.5 x 19 x 19 a.u. The bands obtained with an ordinary supercell calculation with no cutoff (red dashed line) are compared to the bands obtained applying the 1D cylindrical cutoff (black solid line). As it is explained in the text, only the unoccupied levels are affected by the cutoff.

are observed with respect to the supercell calculation. In Fig. 5.4 a Na chain with lattice constant 7.5 a.u. is considered in a cell of 7.5x19x19 a.u., and the effect of the effect of the cutoff on the occupied and unoccupied states is shown. As expected, the occupied states are not affected by the use of the cutoff, since the density of the system within the cutoff radius is unchanged, and the corresponding band is the same as it is found for an ordinary 3D supercell calculation with the same supercell size. However there is a clear effect on the bands corresponding to the unoccupied states, and the effect is larger the higher is the energy of the states. In fact the high energy states, and the states in the continuum are more delocalized, and therefore the effect of the boundary conditions is more sensible about them.

5.4.2 Static polarizability

After the successful analysis of the ground state properties with the cutoff scheme, we have applied the modified Coulomb potential to calculate the static polarizability of an infinite chain in the Random Phase Approximation (RPA). As a test case we have considered a chain made of hydrogen atoms, two atoms per cell at a distance of 2 a.u. The lattice parameter was 4.5 a.u. For this system we have also calculated excited state properties in many-body perturbation theory, in particular the quasiparticle gap in Hedin’s GW approximation (section (3.3)) and the optical absorption spectra in the Bethe-Salpeter framework (section (3.4)) (see subsections below). All
these calculations have been performed in the code \textbf{SELF}. The polarizability for the monomer in the RPA approximation including local field effects is defined as

\begin{equation}
\alpha = - \lim_{q \to 0} \frac{1}{q^2} \chi_{00}(q) \frac{\Omega}{4\pi}.
\end{equation}

(5.29)

where $\chi_{GG'}(q)$ is the interacting polarization function that is solution of the Dyson like equation:

\begin{equation}
\chi_{GG'}(q) = \chi_{0G}^0(q) + \sum_{G''} \chi_{0G''}^0(q)v(q + G'')\chi_{G''G'}(q).
\end{equation}

(5.30)

and $\chi^0$ is the non interacting polarization function obtained by the Adler Wiser expression Eq. (2.17) calculated for $\omega = 0$ that now in reciprocal space reads:

\begin{equation}
\chi_0(q, \omega) = \sum_{i,j} (f_i - f_j) \frac{\langle j | e^{-i(q+G)^r} | i \rangle \langle i | e^{i(q+G)^r} | j \rangle}{\omega - \omega_{ij} + i\eta}.
\end{equation}

(5.31)

$v(q+G)$ are the Fourier components of the Coulomb interaction. The RPA polarizability, Eq. (5.30), is equivalent to Eq. (2.18) formulated in G-space, once $f_{xc}$ is set to 0. Equation (5.29) is nothing else that Eq. (2.13) in Fourier space. In the top panel of Fig. 5.5 we compare the values of the calculated polarizability $\alpha$ for different supercell sizes. $\alpha$ is calculated both using the bare Coulomb $v(q + G) = \frac{4\pi}{|q+G|^2}$ and the modified cutoff potential of Eq. (5.12) (the radius of the cutoff is always set to half the inter-chain distance). The lattice constant along the chain axis is kept fixed. Using the cutoff the static polarizability already converges to the asymptotic value with an inter-chain distance of 25 a.u., while without the cutoff the convergence is much slower, and the exact value is approximated to the same accuracy for much larger cell sizes (beyond the calculations shown in the top of Fig. 5.5). We must stress that the treatment of the divergences in this case is different with respect to the case of the Hartree and ionic potential cancellation for ground-state calculations (i.e. charge neutrality). In fact, while in the calculation for the Hartree and ionic potential the diverging terms are simply dropped by virtue of the neutralizing positive background, here we are treating only the electronic part and the $h$-dependence in Eq. (5.25) can be removed only for the head component by virtue of the vanishing limit $\lim_{q \to 0} \chi^0_{00}(q) = 0$, while for the other $G_z = 0$ components we have to resort to the expression of the finite cylindrical cutoff as in Eq. (5.25). A finite version of the 1D cutoff has been recently applied to nanotube calculations.[Spataru 04b, Spataru 04a] This cutoff was obtained by numerically truncating the Coulomb interaction along the axis of the nanotube, in
Figure 5.5: **Top:** Polarizability per unit cell of an $H_2$ chain in RPA approximation as a function of the supercell volume. The solid line joins the values obtained with the cutoff potential, while the dashed lines joins the values obtained with the bare Coulomb potential. The cutoff radius is 8.0 a.u. The inter-chain distance is indicated in the top axis. **Bottom:** Polarizability of the $H_2$ chain calculated with the finite cutoff potential of Ref.[Spataru 04a]. In abscissa different values of the cutoff length along the chain axis. The dashed straight line indicates the value obtained with the cutoff of Eq. (5.12)
5.4 Results

Figure 5.6: Convergence of the polarizability with respect to the $k$-point sampling along the chain axis obtained with the cutoff potential of Eq. (5.12). In the upper axis it is indicated the maximum allowed length $h$ for each $k$-point sampling used for the calculation of the $G_x = 0$ components by Eq. (5.25).

In addition to the radial truncation. Therefore the effective interaction is limited to a finite cylinder, whose size can be up to a hundred times the unit cell size, depending on the density of the $k$-point sampling along the axis. The cutoff axial length $h$ has to be larger than the expected bound exciton length. This cutoff potential reads:

$$V_{cyl}^{finite}(G) = 4\pi \int_0^R ds s J_0(G s) \int_0^h dt \frac{\cos(G t)}{\sqrt{s^2 + t^2}}$$  \quad (5.32)

and the maximum value of the size of the cutoff axial length $h$ is $2\pi / \Delta k$, where $\Delta k$ is the spacing of the $k$-point grid in the direction of the cylinder axis. Note that the component $(G_x = 0, G_{\perp})$ of this potential can be approximated by Eq. (5.25) and of course the value of $h$ has the same limitation as in Eq. (5.32). In the bottom part of Fig. 5.5 we compare the results obtained with our analytical cutoff (Eq. (5.12)) with its finite counterpart as in Ref. [Spataru 04a] Eq. (5.32). We observe that the value of the static polarizability calculated with the finite cutoff of Spataru et al. oscillates around an asymptotic value, for increasing axial cutoff lengths. The asymptotic value exactly coincides with the value that is obtained with our exact technique cutoff. We stress that we also resort to the finite form of the cutoff only for the diverging of components of the potential, thus we note that there is a clear numerical advantage in using our expression since the cutoff is analytical for all values except $G_x = 0$, and the corresponding quadrature has to be numerically evaluated for these
point only. In Fig. 5.6 is shown the convergences of the polarizability obtained with our cutoff with respect to the \( k \)-points sampling. The sampling is unidimensional along the axial direction. Using 20 \( k \)-points the calculation is already converged. In the upper axis it is also indicated the corresponding maximum allowed value of the finite cutoff length in the axial direction that has been used to calculate the \( G_x = 0 \) component. Finite size effects turn to be relevant also for many-body perturbation theory calculations. For the same test system (linear \( \text{H}_2 \)-chain) we look in the next two subsections to the performance of our cutoff potential for the calculation of the quasiparticle energies in GW approximation and in the absorption spectra in the Bethe-Salpeter framework.

### 5.4.3 Quasiparticles in the GW approximation

Here we show the effect of the modified cutoff potential on the calculation of the quasiparticles energies in GW approximation for the same system studied in section (5.4.2). We first calculate the ground state electronic properties using the DFT code \textit{ABINIT}. These calculation are performed in LDA [Perdew 81] and pseudopotentials [Troullier 91] approximations. An energy cutoff of 30 Hartree has been used to get converged results. The LDA eigenvalues and eigenfunctions are then used to construct the RPA screened Coulomb interaction \( W \) Eq. (2.40), and the GW Self Energy as described in Eq. (3.24). In order to eliminate the spurious interaction between different supercells, leaving the bare Coulomb interaction unchanged along the chain direction, we just introduce the expression of Eq. (5.12) in the construction of \( \Sigma_x \) Eq. (4.16) and \( \Sigma_c \) Eq. (4.17). The integral in the frequency domain of Eq. (4.17) has been performed analytically using the plasmon pole approximation, so the cutoff potential has been used also in the calculation of \( \epsilon_{GG'}^{-1} \) for the the two frequencies needed to fit the expression of Eq. (4.18). As we did for the calculation of the static polarizability, the divergences appearing in the components \( (G_x = 0) \) cannot be fully removed and for such components we resort to the finite version of the cutoff potential Eq. (5.25). In the top panel of Fig. 5.7 the convergence of the quasiparticle gap at the \( X \) point is calculated for different supercell sizes in the GW approximation. A cutoff radius of 8.0 a.u. has been used. When the cutoff potential is used, 60 \( k \)-points along the axis direction has been necessary to get converged results. In the bottom panel of Fig. 5.7 we show the behavior of the quasiparticle gap in function of the cutoff radius We can observe that for \( R_c > 6a.u. \) a plateau is reached and for \( R_c > 12a.u. \) small oscillation appears due to interaction between
Figure 5.7: Top: Convergence of the GW quasiparticle gap for the $H_2$ chain as a function of the cell size, using the bare Coulomb potential (dashed line) and the cutoff potential (solid line). Bottom: Behavior of the GW quasiparticle gap in function of the value of the cutoff radius for a supercell with inter-chain distance of 32 a.u. is showed.

...
addition of an electron (or a hole) in the system induces charge oscillation in the periodic images. It is important to note that the slow convergence is caused by the correlation part of the Self-energy (Eq. (4.17)), while the exchange part is rapidly convergent with respect to the cell size. The use of the cutoff Coulomb potential really improves drastically the convergence as it is evident from Fig. 5.7. Notice that still at 38 a.u. inter-chain distance the GW gap is underestimated by about 0.5 eV. A similar trend (but with smaller variations) has been found by Onida et al. [Onida 95], for a finite system (Sodium Tetramer) using the cutoff potential of Eq. (5.11). Clearly there is a strong dimensionality dependence of the Self-energy correction. The non-monotonic behavior versus dimensionality of the self-energy correction has also been point out in ref. [Delerue 03] where the gap-correction was shown to have a strong component of the surface polarization.

5.4.4 Exciton binding energy: Bethe-Salpeter equation

Starting from the quasiparticle energies we have calculated the optical absorption spectra including electron-hole interactions solving the Bethe-Salpeter equation (3.40). For the discussion below we consider only singlet states and only the resonant part of \( H^{exc} \) (3.44). The approximation of neglecting the coupling part of the Excitonic Hamiltonian is well justified as we will see in the next chapter. The quasiparticle energies entering in the diagonal part of the Hamiltonian (Eq.3.44) are obtained applying a scissor operator to the LDA energies, because in the studied test case the main difference between the Quasiparticle and LDA band structure consists of a rigid energy shift of energy bands. From the solution of the BS equation (Eq.4.20) it is possible to calculate the macroscopic dielectric function from Eq. (3.42), that when only resonant part is considered the imaginary part reduces to:

\[
\epsilon_2(\omega) = 2 \lim_{\eta \to 0} \frac{1}{q^2} \sum_S \text{Im} \left\{ \sum_{v\text{k}} A_S^{v\text{k}} \langle v\text{k} - q| e^{-i\text{q}\cdot\text{r}} |e\text{k}\rangle \right\}^2 \frac{E_S - \omega - i\eta}{E_S - \omega - i\eta},
\]

(5.33)

where the summation runs over all the vertical excitations from the ground state to excited state \( \Psi_s \), \( E_S \) is the corresponding excitation energy and \( \eta \) is a positive infinitesimal. As in the case of GW calculation, in order to isolate the chain, we substitute the cutoff potential of Eq. (5.12) both in the exchange term Eq. (4.21) and in the direct term of the BS equation Eq. (4.22), as well as for the RPA dielectric matrix present in Eq. (4.22). In the top panel of Fig. 5.8 we show the calculated
5.4 Results

Figure 5.8: **Top:** Photo absorption cross section for different supercell volumes. In the legend the inter-chain distances corresponding to each volume are indicated. The intensity have been normalized to the volume of the supercell. The non-interacting absorption spectra and the spectra obtained with the cutoff potential are also included. **Bottom:** exciton binding energy vs supercell volume calculated using the cut off potential (solid line), and the bare Coulomb potential (dashed line).
Figure 5.9: Values of $\epsilon_{00}^{-1}(q_x, q_y)$ in the $q_z = 0$ plane for the $H_2$ chain with an inter-chain distance of 25 a.u., using the bare Coulomb (top) and the cutoff potential (bottom). The axis of the chain is along the x direction.

spectra for different cell sizes together with the non-interacting spectrum, and the spectrum obtained using the cutoff Coulomb potential for an inter-chain distance larger than 20 a.u. and cylindrical cutoff radius of 8 a.u. The scissor operator applied in this calculation is the same for all the volumes and correspond to the converged GW gap. As it is known, the electron-hole interaction modifies both the shape and the energy of the main absorption peak. The present results clearly illustrate that the spectrum calculated without the cutoff slowly converges toward
the exact result. This is highlighted in the bottom panel of Fig. 5.8 where we show the dependency of the exciton binding energy on the supercell volume, the binding energy being defined as the energy difference between the excitonic peak and the optical gap. We observe that the effect of the inter-chain interaction consists in reducing the binding energy with respect to its value in the isolated system. This value is slowly approached as the inter-chain distance increases, while, once the cutoff is applied to the Coulomb potential, the limit is reached as soon as the densities of the system and its periodical images do not interact. If we consider the convergence of the quasiparticle gap and of the binding energy with respect to the cell volume we notice that, if a cutoff is not used, the position of the absorption peak is controlled by the convergence of the BS solution, which, in turn, depends on the (slower) convergence of the GW energies. It is clear from Fig. 5.7 that the use of the cutoff allows us to considerably speed up this bottleneck. The use of our cutoff also has an important effect on the Brillouin zone sampling. In Fig. 5.9 we show the value of $c_{00}^{-1}(q_x, q_y)$ in the $q_z = 0$ plane for a supercell corresponding to an inter-chain distance of 25 a.u. When the cutoff potential is used (bottom panel) the screening is smaller, compared to the case of the bare potential (top panel). Looking at the direction perpendicular to the chain (the chain axis is along the $x$ direction) we see that the dielectric matrix is approximately constant, and this fact allows us to sample the Brillouin zone only in the direction of the chain axis. For both the GW and Bethe-Salpeter calculations a three dimensional sampling of the Brillouin zone is needed to get converged results when no cutoff is used, while a simple one-dimensional sampling can be adopted when the interaction is cutoff.

5.4.5 Comparison between real-space and plane wave codes

We end this section by showing a calculation of the photo-absorption spectra of one monomer of polyacetylene, a finite system performed as a test for the two code employed in this thesis. The absorption spectra is calculated in TDDFT with the ALDA approximation. One calculation is made in real space and real time as described in section (4.1) using the code OCTOPUS, and the polarizability is given by Eq. (2.13). The other one in the supercell approach. In reciprocal space the same quantity is given by Eq. (5.29), and the polarization function in the ALDA
approximation is:

$$
\chi_{G'G}(q, \omega) = \chi_{G'G}^0(q, \omega) + \sum_{G_1,G_2} \chi_{G_1G_2}^0(q, \omega) \left( v(q + G_1) \delta_{G_1G_2} + f_{xc}^{ALDA}(G_2-G_1) \right) \chi_{G_2G'}(q).
$$

$$
(5.34)
$$

Unfortunately the use of a large supercell needed to simulate an isolated system makes the implementation of the effect of $f_{xc}$ in Eq. (5.34) quite delicate in the case of the ALDA approximation. As seen in section (2.1) the ALDA kernel takes the form:

$$
f_{xc}^{ALDA}(r, r') = \delta(r - r') \frac{\partial V_{xc}^{ALDA}(n(r), r)}{\partial n(r)}.
$$

$$
(5.35)
$$

Since in the supercell, as described above, have to be region of the space where the density vanishes, and we have that:

$$
\lim_{n \to 0} \frac{\partial V_{xc}^{ALDA}(n(r), r)}{\partial n(r)} = \infty
$$

$$
(5.36)
$$

the evaluation of the term involving the $f_{xc}$ in Eq. (5.34) cannot be directly calculated as: $\sum_{G_1,G_2} \chi_{G_1G_2}^0 f_{xc}^{ALDA}(G_2-G_1)$ because the Fourier transform of the divergent function $f_{xc}^{ALDA}$ is ill-defined. To overcome this problem we have implemented

Figure 5.10: Calculated photo-absorption spectra at ALDA level of one monomer poly-acetylene molecule using either the real-space real-time code OCTOPUS solving in real time the KS equation (cfr section (2.2.2)) or the plane wave code SELF in configuration space (see text for detail). In the inset the structure of the molecule is shown.
in the code \textsc{Self} the solution of the TDDFT equation in ALDA approximation in the configuration space. Similarly to the BS equation where we have written the polarizability in the form of Eq. (3.36) we can write the polarizability $\chi$ in configuration space as:

$$\chi(n_1,n_2)(n_3,n_4) = \left[H^{ALDA} - I\omega\right]^{-1}_{(n_1,n_2)(n_3,n_4)} \left(f_{n_4} - f_{n_3}\right)$$  \hspace{0.5cm} (5.37)

and calculate the polarizability $\chi$ by diagonalizing the ALDA Hamiltonian. Following the same steps as we have arrived at Eq. (3.44) for the resonant part of the excitonic Hamiltonian, now we have for the ALDA Hamiltonian:

$$H^{ALDA, res}_{(v,c)(v',c')} = H^{dia}_{(v,c)(v',c')} + 2K^x_{(v,c)(v',c')} + K^{ALDA}_{(v,c)(v',c')}$$  \hspace{0.5cm} (5.38)

where $H^{dia}_{(v,c)(v',c')}$ and $K^x_{(v,c)(v',c')}$ are respectively given by Eq. (3.45a) and Eq. (4.21) in reciprocal space, while $K^{ALDA}_{(v,c)(v',c')}$ is given by:

$$K^{ALDA}_{(v,c)(v',c')} = 2 \int d\mathbf{r} d\mathbf{r}' \phi^*_c(\mathbf{r}) \phi_v(\mathbf{r}) f^{ALDA}_{xc}(\mathbf{r}, \mathbf{r}') \phi^*_{c'}(\mathbf{r}') \phi^*_{v}(\mathbf{r}')$$  \hspace{0.5cm} (5.39)

where we have omitted the label $\mathbf{k}$ because for a finite system we have considered only the $\Gamma$ point. The coupling part of the Hamiltonian is written analogously to Eq. (3.46) inverting the indexes $\{v',c'\} \rightarrow \{c',v'\}$. The term $K^{ALDA}_{(v,c)(v',c')}$ is evaluated in real space, performing the Fast Fourier Transform in order to obtain the KS wave-functions $\phi_i(\mathbf{r})$. It is important to note here that at difference of the BS equation, in TDDFT the diagonal and the off-diagonal blocks are of the same order of magnitude, and the off-diagonal blocks cannot be neglected. The obtained results are shown in Fig. 5.10, together with the atomic structure of the simulated molecule. The real space calculation has been done in a spherical simulation box of 13.5 a.u. radius and a spacing of 0.4 a.u.. The total time of the simulation was 15 fs with a time step of 0.001 fs. For the plane waves calculation we adopted a cubic supercell with side of 30 a.u. and a spherical cut coulomb potential Eq. (5.11) with a cutoff radius of 12 a.u. The ALDA Hamiltonian Eq. (5.38) was constructed including conduction-valence pairs up to 27 eV (240 bands) and in the exchange part have been included 10000 plane waves ($G^2/2=10$ Ry), in order to get converged results. We found a good agreement between the two calculations, in particular for the first and more relevant peak.
Chapter 5. An exact Coulomb cutoff technique for supercell calculations
Part III

Applications
Over the last years TDDFT has emerged as a very successful framework to describe the optical spectra of small nanostructured materials, thanks to its simplicity and moderate computational cost. It has been shown to work very well for the description of electronic excitations of a large set of molecular systems [Furche 05]: first and second row elements as well as noble and early transition metal systems. Another major area of application is clusters, covalent and metallic, including Met-Cars [Martinez 04]. Only recently the TDDFT has started to be used for studying the optical response of some biomolecules and photo-biology problems e.g. chlorophylls [Sundholm 00, Sundholm 03], flavins [Neiss 03], nucleic acid bases [Tsolakidis 05, Shukla 04], and protonated Schiff base of retinal [Tachikawa 04]. Therefore, we think it is a promising tool for the description of excited-state biological processes. It is still perhaps too soon to discuss the general level of accuracy of TDDFT when applied to biomolecules, especially when dealing with van der Waals complexes [von Lilienfeld 04] and charge-transfer excitations [Dreuw 03]. Furthermore, as the field is quite recent, we can still expect rapid methodological developments, in particular the derivation of better exchange-correlation functionals. However, the existing results are very promising, and pave the way for a broader application of TDDFT in Biochemistry. Besides the spectacular advances in the characterization of structural and dynamical properties of complex biomolecules by a combination of quantum-mechanical and classical-molecular mechanics methods (QM/MM) [Brunger 88, Laio 02], the theoretical description of the interaction of these molecules with external time-dependent fields is very much in its infancy. In particular, processes related to vision and photosynthesis rely on a subtle interplay between optical absorption in the photo-active center and its decaying mechanism through the coupling to the internal vibrational modes of the molecule, including isomerization processes as well as coupling to the environment (hosting protein and solvent). In this chapter we apply the TDDFT, in its real time real space implementation as described in section (2.2.2) to study optical properties for two paradigmatic
systems of broad biological interest. In section (6.1) we discuss the excited states properties of DNA bases and some assemblies of bases in different configurations. In this work in particular we have studied paired bases in Watson Crick and in stacked configurations and a tetramer constituted of two paired bases. This study has permitted to analyze the impact of the different types of interaction (hydrogen bonding and π-stacking) in the absorption spectra of such systems. The study of such big systems has been feasible with the real-time real-space implementation of the TDDFT, otherwise too much computationally demanding for the traditional methods of quantum chemistry. Next, in section (6.2) we will discuss the absorption spectra of the green fluorescent protein (GFP), that we have studied within a quantum-mechanical molecular mechanics (QM/MM) and TDDFT approach. The calculations turns to be in an excellent agreement with the experiments and have permitted to relate the shape of the absorption spectra with the presence of two different form, protonated and deprotonated, of the chromophore.

6.1 Excited states of DNA bases and their assemblies†

Optical absorption spectroscopy is especially important for DNA and DNA-based compounds. These techniques were extensively applied in the last decades to these systems to characterize their structural and dynamical properties [Ruzsicska 95, Hernández 04a, Daniels 76]. Traditionally, DNA molecules have always retained a special place in scientific investigation, for biological/medical issues. Moreover in the last years, DNA is also attracting interest for several potential applications in the field of nanotechnology, due to its stability (in solution), to its one-dimensional character, and to the regular π-stacking, along with the unique properties of self-assembling and recognition [Porath 04, Endres 04, Nalwa 05, Coehn 05, Di Felice 02]. In relation to nanotechnology, the determination and interpretation of the electronic properties of nucleobases and of DNA helical arrangements are an extremely valuable foreword, and notable multidisciplinary efforts are currently devoted to such goals: we refer the reader to recent reviews about electronic struc-

† This section is largely an adaptation of the article: D. Varsano, R. Di Felice, M.A.L Marques and A. Rubio: Excited states of DNA bases and their assemblies accepted in J. Phys. Chem. B (2006). As such, the reported work includes collaboration of the rest of the authors of the article. This paper can be downloaded from cond-mat/0603086
6.1 Excited states of DNA bases and their assemblies

ture calculations and possible charge motion behaviors [Porath 04, Di Felice 05]. Furthermore, the knowledge of the electronic properties, excited state lifetimes, and ultra-violet (UV) absorption spectrum is of paramount important for our understanding, e.g., of the crucial phenomena of UV radiation-induced DNA damage [Kraemer 97, Odom 01, Hernández 05]. From this brief preamble, it is clear that the full characterization of the optical properties of such DNA complexes is of great interest. In order to relate the optical properties of the nucleic acids to their structure, spatial conformation, and type of intra-molecular interactions, a valuable preliminary step is to gain insight into the excited-state properties of their building blocks, namely the monomeric bases, and to understand the role of hydrogen-bonding and stacking when these monomeric units form complex assemblies. In their natural environment, the DNA bases are paired via hydrogen-bonds in the so called Watson-Crick scheme [Watson 53], and are covalently bonded to the sugar-phosphate backbone. The hydrogen-bonded base pairs interact with each other in the typical helical arrangement by inter-plane van der Waals forces [Hall 96], mediated by the solvent and counter-ions. To disentangle how the different interactions control the DNA dynamics upon light absorption, it is important to infer how the isolated nucleic acid spectra is modified by their mutual interaction in the different spatial conformations of DNA-assemblies. This is the goal of the work presented in this section: To provide a systematic study of the stacking and H-bonding interaction effects in the optical spectra of molecular complexes formed with isolated DNA-bases. As mentioned in the introduction of this chapter we undertake this task by means of time-dependent-density functional (TDDFT) calculations. The present study should be considered as a first step toward the understanding and control of the excited state properties of real DNA based systems, including solvation and environment effects to a later stage. Before studying very complex biological-based DNA complexes it is mandatory to test the performance and predictive power of TDDFT for DNA-based systems. One of the aims of the present work is to provide first-principles calculations of simple DNA-based systems that can be used as reference for future developments and studies. This reference set includes the isolated DNA bases, hydrogen bonded Watson-Crick pairs, stacked bases pairs, and a GC stacked dimer. For the isolated DNA bases there are plenty of experimental and theoretical results concerning their optical response. We do not carry out a full systematic analysis of all the published data for the isolated DNA-bases, but only those more pertaining to our investigation. The wide variety of computational tools applied to nucleobases ranges from single excitation configu-
Chapter 6. Optical spectroscopy of biological chromophores

Correlation interaction (CIS), to complete active space 2nd-order perturbation theory (CASPT2), and includes other approaches such as multireference perturbation configuration interaction (CIPSI). A review of the performance of such methods on the nucleobases is reviewed in Ref. [Hernández 04a], as well as relevant experimental data can be found in Refs. [Fulscher 97, Fulscher 95, Lorentzon 95]. Despite the large number of works on the excited states of isolated DNA bases, there are limited number of studies on base pairs and base assemblies due to their complexity. Shukla and Leszczynski studied adenine-uracil [Shukla 02a], adenine-thymine (AT) and guanine-cytosine (GC) in the Watson-Crick configuration [Shukla 02b] at CIS the level; Sobolewski and Domcke [Sobolewski 04] studied the low lying energy part of the spectrum of GC base pairs with the more sophisticated CASPT2 technique; and Wesolowski [Wesolowski 04] used an embedding method to study the lowest excited state of the GC and AT pairs. Very recently, Tsolakidis and Kaxiras [Tsolakidis 05] computed the whole absorption spectra of the GC and AT pairs in different tautomeric forms of the nucleic acid bases in TDDFT framework. Moreover, very few studies exist on the excited state properties of bases in a stacked configuration: Jean and Hall studied fluorescent properties of dimers of 2-aminopurine stacked with DNA bases [Jean 01] in different forms and stacked trimers containing 2-aminopurine [Jean 02], showing the relevance of the stacked geometries in the excited state properties and in the character of the excited state transitions. To the best of our knowledge, the present results are the first ab-initio calculations dealing with stacked natural bases. Still we remark that the present results are for free standing nucleoacid-complexes, i.e., not including solvation effects. These effects are known to be more important for $n\pi^*$ than $\pi-\pi^*$ type transitions [Mennucci 01, Mishra 00, Shukla 00, Fulscher 97, Shukla 02a, Shukla 02b].

This section is organized as follows: In section (6.1.1) we provide the details used to get the structures and to compute the optical properties. In section (6.1.2) we present our results for the isolated gas-phase nucleobases, i.e., guanine, cytosine, adenine, thymine, and uracil, (G, C, A, T, and U, respectively) and compare with the experiments and previous calculations existing in literature. In order to understand the role of hydrogen-bonding in shifting and modifying the spectral features, we show, in section (6.1.3), results for H-bonded Watson-Crick GC and AT base pairs (labeled GC$_H$ and AT$_H$, respectively). In section (6.1.4) we present results for a GC stacked dimer (labeled GC$_S$) that mimics the arrangement between C and G in two consecutive planes in the real DNA double helix. We also discuss the relative roles of $\pi$-stacking and hydrogen bonding in the optical absorption of
a stacked quartet made of two adjacent Watson-Crick GC pairs as in A-DNA [labelled d(GC)], that combines hydrogen-bonding and π-stacking.

### 6.1.1 Computational Framework

**The structures**

The atomic configurations of the studied systems were obtained performing different relaxations, as in the case of the GFP, with the following procedure. The starting atomic coordinates of the isolated DNA bases and of the AT<sub>H</sub> pair were derived from standard structural parameters for DNA [Arnott 72, Arnott 74], whereas for the systems GC<sub>H</sub>, GC<sub>s</sub>, and d(GC) we extracted the simulated fragments from a high-resolution X-ray crystal structure of A-DNA [Gao 99], after a classical force-field structural adjustment. The crystal is formed by short helices of double stranded DNA with the sequence d(AGGGGCCCT), a model for poly(dG)-poly(dC) DNA showed in Fig. 6.1. Firstly we used the CHARMM package [Brooks 83, MacKerrel 98] to assign the hydrogen coordinates (absent in the X-ray PDB file) and to perform a raw relaxation of the entire structure. Next from this grossly relaxed polymer we extracted the H-bonded and stacked GC fragments, that have been subsequently relaxed by quantum simulations in DFT framework. The simulations allow us to have a complete set of base configurations that could be used to perform configurational sampling and extract structural broadening effects, anyway the analysis of this issue is left for a future work. The DFT structural optimization was carried out using the B3LYP/6-31++G(d,p) exchange-correlation functional for the isolated bases and GC assemblies, and the PW91 functional [Perdew 92] for the AT<sub>H</sub> pair. This latter functional was widely tested in guanine-rich systems [Calzolari 04a, Calzolari 04b, Zhang 04], and yields a similar accuracy for AT<sub>H</sub> pairs and stacked pairs. Note here that all sys-

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Figure 6.1: X-ray structure of A-DNA (PDB:400d) used as starting reference for base assemblies structures.
tems studied in the present work correspond to bases in the gas phase and the effect of a solvent may be crucial when comparing the computational results with experimental data [Mennucci 01, Mishra 00]. Furthermore, the sugar-phosphate backbone was neglected. This restriction should not be relevant in the energy range we are interested in (3–7.5 eV), as the sugar and the phosphate contribution to the absorption spectra only starts to be important above 7.0 eV.

The spectra

The optical absorption spectra of DNA bases and base pairs were computed at TDDFT level with the code OCTOPUS [Marques 03a]. The method has been described before in section (2.2.2) and the numerical implementation in section (4.1). For the exchange-correlation potential \( v_{xc} \) we employed the local density approximation (LDA) with the Perdew-Zunger parametrization [Perdew 81]. In the case of the isolated guanine base, we also performed the time propagation with the generalized gradient approximation (GGA) PW91 [Perdew 96] \( v_{xc} \) functional. As expected [Marques 01], no substantial differences were detected between the two parameterizations. Therefore, the rest of the calculation has been performed with the LDA functional that is numerically the most stable. Anyway it is important here to note that in spite of the equivalence encountered in the photo-absorption cross-section of gas-phase guanine by using these two functionals, which is sufficient for our purposes to justify the LDA option, one has to be extremely careful in general in the choice of \( v_{xc} \). For instance, it was shown that for processes that involve charge transfer mechanisms, like fluorescence in base pairs, it is important to have the correct asymptotic behavior of the exchange-correlation functional (See, e.g. [Grimee 03]). Concerning technical details: We used a real-space grid made of overlapping spheres centered around each nucleus with a radius of 4 Å. All quantities were discretized in a uniform grid with spacing 0.23 Å. The time-step for the time evolution was 0.0066 fs (which ensures stability in the time-dependent propagation of the KS wave functions) and the total propagation time was at least 20 fs. Such simulation parameters ensure well converged absorption spectra up to about 8 eV. The energy resolution, dictated by the total simulation length by \( \Delta E \sim h/T \), is better than 30 meV. This set the lower limit for the linewidth of the calculated spectra, any additional broadening is intrinsic to the system. The electron-ion interaction (both in the time-dependent and time-independent DFT calculations) was modeled by norm-conserving pseudopotentials [Troullier 91]. To compare with ex-
6.1 Excited states of DNA bases and their assemblies

Figure 6.2: Dipole strength function of Cytosine along the axis perpendicular to the base plane, calculated through the real-time propagation (blue solid curve) and in the frequency domain [Casida 95] (green dashed curve). An artificial broadening of 0.15 eV was adopted as an eye help to compare both time and frequency domain spectra. Note that we can distinguish the $n\pi^*$ character in an indisputable way only for the lowest energy peak. At higher energy the $n\pi^*$ character is less pure, due to the mixing of a large number of transitions. This fact is illustrated here for cytosine, but observed for all the investigated nucleobases.

Experiments where the molecules are not aligned with respect to the applied field, we need to average the response along the three Cartesian axis [cf. Eq. (2.14)]. This result can be directly compared to other available data and used to discriminate among different nucleoacid conformations. However, the analysis can be taken even further: in the case of planar molecules (isolated bases, GC$_H$, AT$_H$) one can easily distinguish between in-plane and out-of-plane transitions. While the former are prevalently $\pi\pi^*$ and have large oscillator strengths, the latter are much weaker (by one or two orders of magnitude) and are usually hidden under the stronger signals. In order to unveil the character of the weak transitions, the time-domain analysis is not sufficient: Thus, we also performed linear response calculations in the frequency domain [Casida 95], as described in section (2.2.1) for all planar structures (isolated bases, GC$_H$, and AT$_H$ pairs). In this formalism, several pairs of occupied/unoccupied orbitals participate in each excitation with different weights: it is then possible to qualitatively assign to each excitation the predominant character
of the contributing transitions (see Eqs. 2.28-2.30). In Fig. 6.2 we show an example of the transition character of spectral features, derived from our frequency analysis of cytosine. The dipole strength function of cytosine along the direction perpendicular to the base plane, obtained by both the time-domain and frequency-domain techniques, is plotted against energy. The agreement encountered between the two techniques turns out to be very good in all the sampled energy range. For all other planar systems, we present the analysis of the transition characters obtained in a similar way, but without explicitly showing the figures for the spectra obtained by frequency-domain TDDFT. We note that in the frequency-domain the transition are delta functions, in order to make a fair comparison with the time-domain propagation we have artificially broadened both spectra using a lorentizian function of 0.15eV width. Note that for the rest of the spectra showed in the paper obtained with the time-propagation scheme, we didn’t add any additional broadening and the resolution of 30meV is fixed by the duration of the time evolution. Any additional broadening comes from the coupling of the exciton state to other excitations (e.g. Landau damping). It is well known that LDA may be grossly wrong in the description of H-bonds: that is why different gradient-corrected functionals were used to relax the geometries. However we also know that once the geometry is given the LDA and GGA furnish very similar results for the excitations, therefore we stick to the LDA functional for simplicity. We are confident this is a reasonable approximation, indeed in the the discussed above for guanine, different functionals do not yield significant differences as far as the optical excitations are concerned.

6.1.2 Isolated gas-phase nucleobases

In this section we present the calculated absorption spectra for the five isolated nucleobases. Both the purines and the pyrimidines exist in nature in different tautomeric forms. We limited our calculations to the 9H keto form of guanine, and to the 9H amino form of adenine. The latter tautomer is the one present in DNA and RNA polymers, and is therefore the most relevant regarding the adenine properties in nucleic acids.

Cytosine

The computed total and perpendicular photo-absorption cross sections of cytosine are shown in Fig. 6.3. The positions of the spectral peaks are reported in Table 6.1
6.1 Excited states of DNA bases and their assemblies

Figure 6.3: Calculated photo-absorption cross section of isolated Cytosine. The solid blue (dashed yellow) line is the signal averaged along the three real-space axes (projected onto the axis perpendicular to the base plane). Insets: HOMO (left) and LUMO (right) Kohn-Sham wave functions. The cyan (magenta) isosurfaces represent positive (negative) charge values. Different atoms are indicated with different colors: carbon (green), nitrogen (blue), oxygen (red), hydrogen (white).

Table 6.1: Vertical excitations energies (eV) calculated for Cytosine, compared with averaged experimental values and selected computational results. The columns correspond to: (a) this work; (b)Ref. [Tsokakidis 05]; (c)Ref. [Fulscher 95]; (d)Ref. [Shukla 04]. The experimental absorption and CD values, along with the original references, are collected in Ref.[Fulscher 95].

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<th>CASPT2(^{(c)})</th>
<th>TDDFT(^{(d)})</th>
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together with other selected sets of data that represent the state-of-the-art performance of experimental and computational techniques on cytosine. For what concerns the transition energies, from an overall glance at Table 6.1 it emerges that there is a rather good agreement of our results with those obtained in Ref. [Tsolakidis 05], and a poorer matching with the outcome of B3LYP-TDDFT based on the GAUSSIAN98 suite of codes of Ref. [Shukla 04], and of CASPT2. None of the computational data is in perfect accord with experiment. Therefore, a selection of the best theoretical approach on the basis of the comparison between theory and experiment is hindered. Our agreement with experimental values is much more satisfactory in the high-energy than in the low-energy regime. If we turn our attention to the relative oscillator strengths between the various peaks, then the agreement with the data of Ref. [Tsolakidis 05] is not so perfect: we encounter differences in the distribution of oscillation strengths in the high-energy range of the spectrum. We will see later that these high energy discrepancies also appear in the spectra of the other nucleobases and can be traced to the limitations of the localized basis set used in Ref. [Tsolakidis 05], and absent in the present work due to the use of a real-space grid. Combining the time-domain spectra with the frequency-domain analysis, we can describe the spectral peaks in terms of transitions between electron states. Fig. 6.2 shows an $n\pi^*$ transition at 4.3 eV in the perpendicular spectrum, not clearly discernible in Fig. 6.3 because of the low intensity of the perpendicular signal. This means that the lowest energy peak at 4.18 eV in the averaged spectrum (Table 6.1), absent in the perpendicular polarization, must have a $\pi\pi^*$ character. The fact that the first optical excitation in cytosine is $\pi\pi^*$-like was predicted in all recent computational studies. The spacing between the lowest $\pi\pi^*$ excitation and the $n\pi^*$ transition computed by us is 0.12 eV: this value turns out to be in good agreement with the results of B3LYP-TDDFT [Shukla 04] and CIS [Shukla 99], whereas CASPT2 calculations [Fulscher 95, Merchan 03] predict a larger spacing between the two excitations. A smaller spacing was found with B3LYP-TDDFT [Ismail 02].

Uracil and thymine

The computed total and perpendicular photo-absorption cross sections of thymine and uracil are shown respectively in Fig. 6.4 and Fig. 6.5. The positions of the spectral peaks are reported in Tables 6.2 and 6.3. The spectra of the two bases U and T are very similar, both in the number of peaks and spectral energies. A fairly good agreement is encountered with averaged experimental data, as well as
6.1 Excited states of DNA bases and their assemblies

Figure 6.4: Calculated photo-absorption cross section of isolated Thymine. The solid blue (dashed yellow) line is the signal averaged along the three real-space axes (projected onto the axis perpendicular to the base plane). Insets: HOMO (left) and LUMO (right) Kohn-Sham wave functions. The cyan (magenta) isosurfaces represent positive (negative) charge values. Different atoms are indicated with different colors: carbon (green), nitrogen (blue), oxygen (red), hydrogen (white).

Table 6.2: Vertical excitations energies (eV) calculated for Thymine, compared with average experimental values and selected calculations. The columns correspond to: (a) this work; (b) Ref. [Tsokakis 05]; (c) Ref. [Lorentzon 95]; (d) Ref [Shukla 04]. The experimental absorption and CD values, along with the original references, are collected in Ref.[Lorentzon 95], except the second experimental band that is taken from Refs.[Miles 67, Sprecher 77].

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<th>Exp.</th>
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<th>CASPT2$^{(c)}$</th>
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Figure 6.5: Calculated photo-absorption cross section of isolated Uracil. The solid blue (dashed yellow) line is the signal averaged along the three real-space axes (projected onto the axis perpendicular to the base plane). Insets: HOMO (left) and LUMO (right) Kohn-Sham wave functions. The cyan (magenta) isosurfaces represent positive (negative) charge values. Different atoms are indicated with different colors: carbon (green), nitrogen (blue), oxygen (red), hydrogen (white).

Table 6.3: Vertical excitations energies (eV) calculated for Uracil, compared with average experimental values and selected calculations. The columns correspond to: (a) this work; (b) Ref. [Lorentzon 95]; (c) Ref. [Shukla 04]; (d) this band was obtained in CD spectra and it was argued that it exhibits nπ* character. The experimental absorption and CD values, along with the original references, are collected in Ref.[Lorentzon 95], except the second experimental band that is taken from Refs.[Miles 67, Sprecher 77].
with TDDFT [Tsolakidis 05, Shukla 04] and CASPT2 [Lorentzon 95] computational data. All previous calculations, either in the TDDFT framework or with quantum chemistry methods, predict the lowest transition to have an $n\pi^*$ character in vacuo. We agree with this assignment for uracil (the perpendicular signal is not visible at 4.69 eV in Fig. 6.5 due to the weak intensity). In the case of thymine, we do not find any appreciable signal perpendicular to the base plane contributing to the peak at 4.54 eV. However, this is consistent with TDDFT calculations of Ref. [Shukla 04] and CASPT2 of Ref. [Lorentzon 95], as they indeed report $n\pi^*$ transitions with extremely small oscillation strengths (1e-4–1e-6), unresolved by us. The character of the band at 4.9–5.2 eV for uracil and at 5.0–5.1 eV for thymine is not yet clear: the absorption spectra of uracil compounds [Clark 65] and circular dichroism experiments [Miles 67] indicate that it is due to a $\pi\pi^*$ transition. However, such $\pi\pi^*$ character has not been confirmed by magnetic circular dichroism [Voelter 68] and polarized absorption spectra experiments [Stewart 63, Stewart 64, Fucaloro 71, Eaton 70]. Lorentzon and coworkers [Lorentzon 95], by performing calculations at the CASPT2 level, suggest that this band has $n\pi^*$ origin: they arrived at this conclusion by correcting their computed values with a 0.5 eV blue-shift due to the solvent. A similar conclusion was reported for uracil by Shukla and coworkers [Shukla 00], who performed CIS calculations taking the solvent into account with a polarizable continuum model. However, more recently, Shukla and Leszczynski [Shukla 04] using B3LYP-TDDFT reported only a $\pi\pi^*$ transition at 5.17 eV for uracil and at 4.96 for thymine in the energy range under consideration. In our work, we do not detect any absorption in the direction perpendicular to the base-plane in this energy range, whereas peaks at 5.24 eV for T and at 5.25 eV for U are found, with considerable oscillator strength induced by light polarized in the plane of the molecule. Therefore, our results indicate that the second band is most likely to have a $\pi\pi^*$ character.

**Adenine**

The computed total and perpendicular photo-absorption cross sections of 9H-adenine are shown in Fig. 6.6. The positions of the spectral peaks are summarized in Table 6.4 and compared with other available theoretical and experimental data. An excellent agreement with other LDA-TDDFT computed values [Tsolakidis 05] is observed, regarding both the peak energies and the relative oscillation strengths. Slight discrepancies occur only in the high energy range, as these are most likely due to differences in the technical details adopted in the calculations (e.g., the basis sets).
Figure 6.6: Calculated photo-absorption cross section of isolated Adenine. The solid blue (dashed yellow) line is the signal averaged along the three real-space axes (projected onto the axis perpendicular to the base plane). Insets: HOMO (left) and LUMO (right) Kohn-Sham wave functions. The cyan (magenta) isosurfaces represent positive (negative) charge values. Different atoms are indicated with different colors: carbon (green), nitrogen (blue), oxygen (red), hydrogen (white).

Looking at the spectrum in the direction perpendicular to the base plane, we can distinguish four prevalently $n\pi^*$ transitions in the energy range 4.10–4.79 eV, that are hidden in Fig. 6.6 because of their tiny oscillator strengths. We find that the lowest excitation has mainly $n\pi^*$ character and is very close in energy to the first $\pi\pi^*$ transition (forming the peak at 4.51 eV). This result is in agreement with resonant two-photon ionization and laser induced fluorescence spectroscopy of jet cooled adenine [Kim 00], provided that the adiabatic transition energies follow the same trends as the calculated vertical ones. Our findings also agree qualitatively with frequency-domain B3LYP-TDDFT [Shukla 04] and CIPSI [Mennucci 01, Sobolewski 02] calculations, whereas CASPT2 [Fulscher 97] and CIS [Holmen 97, Broo 98, Mishra 00] yield the reverse order. Given the small energy difference between the two transitions we can conclude that the overall qualitative agreement is satisfactory. Proceeding to higher energies, we find the second $\pi\pi^*$ peak 0.37 eV after the first one. Experiments indicate [Holmen 97, Callis 64, Clark 95] that the low energy portion of the adenine photo-absorption spectrum consists of two closely spaced


\begin{center}
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Exp. & TDDFT\textsuperscript{(a)} & TDDFT\textsuperscript{(b)} & CASPT2\textsuperscript{(c)} & TDDFT\textsuperscript{(d)} \\
\hline
4.59 & 4.51 & 4.51 & 5.13 & 4.94 \\
4.8-4.9 & 4.88 & 4.95 & 5.20 & 5.21 \\
5.38 & 5.49 & 5.58 & & \\
5.7-6.1 & 5.72 & 5.79 & 6.24 & 5.93 \\
 & 6.49 & 6.63 & & 6.16 \\
6.81 & 6.76 & 6.92 & 6.99 & \\
 & 7.09 & 7.47 & & \\
7.73 & 7.39 & 7.81 & 7.57 & \\
\hline
\end{tabular}
\end{center}

\textbf{Table 6.4:} Vertical excitations energies (eV) calculated for Adenine, compared with averaged experimental values and selected calculations. The columns correspond to: (a) this work; (b) Ref. [Tsolakidis 05]; (c) Ref. [Fulscher 97]; (d) Ref. [Shukla 04]. The experimental absorption and CD values, along with the original references, are collected in Ref.[Fulscher 97].

\pi\pi^* transitions. Holmén and coworkers showed by linear dichroism that those two peaks are separated by 0.26eV. This value is in reasonable agreement with our results and with other TDDFT calculations [Mennucci 01, Tsolakidis 05], while other computational results obtained with different techniques predict a closer energy spacing. On the other hand, measured spectra indicate that the lowest energy transition has a smaller oscillator strength than the subsequent one: such an evidence is consistent with the CASPT2 and CIPSI results, whereas TDDFT simulations [Tsolakidis 05] yield an inverse ordering of oscillator strengths in the first two peaks (see Fig. 6.6). Concerning other \(n\pi^*\) transitions, there is experimental evidence by circular [Sprecher 77, Brunner 75] and linear [Holmen 97] dichroism of a signal around 5.4eV. Our calculation is also able to reveal a signal in this range. However, the agreement with the experiment for the \(n\pi^*\) transitions should be considered with caution, because of their high sensibility to the effect of the solvent (neglected in our calculations) and exchange-correlation functional.

\textbf{Guanine}

To conclude the presentation of the results for the isolated DNA bases, we show in Fig. 6.7 the computed total and perpendicular photo-absorption cross sections of 9H-guanine. The positions of the spectral peaks are summarized in Table 6.5 and
compared with other available data. The excitation energies are in good agreement with the averaged experimental data and with the results of Ref. [Tsolakidis 05]. Small differences are encountered in the high energy region of the spectrum in the relative oscillator strengths of the peaks at 6.22 eV and 6.67 eV, while the low energy region is in perfect agreement. Again, we attribute the discrepancies at higher energies to the basis set used in Ref. [Tsolakidis 05]. In the region from 5 to 6 eV we also find very weak peaks that are not observed experimentally. Regarding the out-of-plane spectrum, we find one peak at 4.47 eV that has a purely $n\pi^*$ character. Thus, the first $n\pi^*$ transition has a higher energy than the first $\pi\pi^*$ transition found at 4.40 eV (see Table 6.5). This attribution is consistent with previous CASPT2 [Fulscher 97], CIS [Shukla 00], and B3LYP-TDDFT [Hernández 04b] calculations. The results of our calculations performed in TDDFT framework with the real-space real-time scheme [Marques 03a] of the excitation spectra of DNA bases and uracil in the gas phase show a satisfactory agreement with the experimental data and with other computational approaches, especially for the most intense...
6.1 Excited states of DNA bases and their assemblies

<table>
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<tr>
<th>Exp.</th>
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Table 6.5: Vertical excitations energies (eV) calculated for Guanine, compared with averaged experimental values and selected calculations. The columns correspond to: (a) this work; (b) Ref. [Tsolakidis 05]; (c) Ref. [Fulscher 97]; (d) Ref. [Shukla 04]. The experimental absorption and CD values, along with the original references, are collected in Ref.[Fulscher 97].

peak above 6 eV. In particular, good agreement is found with recent LDA-TDDFT calculations using a localized-basis set [Tsolakidis 05]. Minor differences are found regarding the distribution of the oscillator strengths in the high energy range of the spectra. Such discrepancies can be ascribed to the different basis sets used in the calculations: a uniform grid in real space in this work, and a set of localized atomic orbitals in Ref. [Tsolakidis 05]. Regarding the more problematic $n\pi^*$ transitions, we found that the weak perpendicular signal is sometimes hidden below the in-plane signal. In the cases where the $n\pi^*$ transitions can be detected, we found the correct relative ordering between $n\pi^*$ and $\pi\pi^*$ peaks, as compared with other TDDFT calculations performed in the frequency domain. Another interesting trend is the relative ordering among different nucleobases for what concerns the first $\pi\pi^*$ transition. For this feature, supersonic jet experiments report $C < G < A$ [Kim 00, Mons 02, Nir 02]. We indeed find that ordering in our first-principles calculations, i.e. the first excitation at 4.18 eV for cytosine, 4.40 eV for guanine and at 4.52 eV for adenine. Last, we note that our calculations give the expected characters of the Kohn-Sham orbitals of the different bases (see insets in Figs. 6.3-6.7): the LUMO has $\pi$ character for all the nucleobases, whereas the
HOMO is \( \pi \)-like for the purines and \( \sigma \)-like for the pyrimidines, with a high charge density around the oxygen atoms in all cases.

### 6.1.3 Watson-Crick pairs \( \text{GC}_H \) and \( \text{AT}_H \)

Now we turn the discussion to the standard assembly of DNA bases, namely the Watson-Crick pairing. Figure 6.8 shows the calculated TDDFT spectra of H-bonded \( \text{GC}_H \) and \( \text{AT}_H \) pairs (left) and the spectra resolved in the direction perpendicular to the basal plane (right). The sum of the photo-absorption cross sections from the isolated component nucleobases is also shown (indicated by G+C and A+T), to reveal the effects induced by H-bonding in the Watson-Crick pairs. The peaks observed in the spectra are also listed in Table 6.6 for a more detailed analysis. Figure 6.9 illustrates the isosurface plots of the HOMO and LUMO, which are the single-particle orbitals more important for the optical transitions in the energy range discussed here. In both pairs, the HOMO is localized at the purine and the LUMO at the pyrimidine. The HOMO-LUMO gap computed by us at DFT level is 1.93 eV and 3.07 eV for the \( \text{GC}_H \) and \( \text{AT}_H \) pairs, respectively.

We focus our analysis on the most evident features induced by H-bonding base pairing, that are:

i. a small shift found for the lowest frequency peaks;

ii. the hypochromicity (intensity decrease) at high frequencies;

iii. an overall blue-shift of the spectrum for light polarized perpendicular to the pair.

The relaxed structure of the \( \text{GC}_H \) pair is practically planar. The shape of the total photo-absorption spectrum of the hydrogen-bonded \( \text{GC}_H \) pair remains rather similar to the linear superposition of the isolated bases (cf. the top left panel of Fig. 6.8). The first \( \pi\pi^* \) peak at 4.29 eV is composed of the first excitation of cytosine and the first excitation of guanine. We note a slight redshift of this peak with respect to the first peak in the red curve: this effect is the combination of a blue-shift by about 0.1 eV of the first cytosine peak and a comparable redshift of the first guanine peak. Such finding is in qualitative agreement with a CASPT2 calculation by Sobolewski and Domcke [Sobolewski 04] and by a calculation performed by Wesolowski [Wesolowski 04] by embedding methods. For the second \( \pi\pi^* \)
transition at 4.72 eV the situation is reversed: The peak is blue-shifted with respect to the superposition of isolated G and C. This shift results from a blue-shift of the second guanine peak and a red-shift of the second cytosine peak. In the high-energy spectral range, we remark that the effect of the pairing does not change the position of the brightest peak at 6.17 eV, which has both G and C components. However, the intensity of this peak is depressed (hypochromism) by about 30% with respect to the free monomers. Above this energy the spectrum results much more changed. Looking at the direction perpendicular to the plane of the GC\textsubscript{H} pair (Fig. 6.8 top right panel), we observe an overall blue-shift of the spectrum. In particular, the first peak is shifted upward by 0.48 eV. This behavior reflects the well known uplifting of $n\pi^*$ excitation energies in hydrogen-bonding environments, already pointed out by other authors [Callis 83, Brealey 55], and appears naturally from our first-principles
Table 6.6: Vertical excitation energies (eV) for Watson-Crick GC_H and AT_H pairs, compared to other calculations. The columns correspond to: (a) this work; (b) Ref. [Tsolakidis 05]; (c) Ref. [Sobolewski 04] (cf. also the results of Shukla and Leszczynski [Shukla 02a]); (d) Charge transfer transition.

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<th>GC_H</th>
<th>AT_H</th>
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<td>TDDFT(a)</td>
<td>2.44</td>
<td>2.37</td>
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<td>TDDFT(b)</td>
<td>3.14</td>
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<tr>
<td>CASPT2(c)</td>
<td>3.94</td>
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simulation. For the AT_H pair, Table 6.6 highlights an overall good agreement with a recent LDA-TDDFT calculation [Tsolakidis 05]. Small differences can be reasonably imputed to the different structure obtained upon relaxation. We find an almost planar geometry, in agreement with Shukla and Leszczynski [Shukla 02a], while Tsolakidis and Kaxiras [Tsolakidis 05] find a propeller structure. As in the case of the GC_H pair, the overall spectrum of AT_H is quite similar to the linear combination of the spectra of the isolated A and T bases. A small blue-shift, by ~0.1 eV, is encountered in the low-energy range (roughly below 6 eV) with respect to the superposition of isolated bases. In the high-energy part of the spectrum, we observe an enhancement of the strength with respect to isolated adenine and thymine for the peak located at 6.78 eV, and a reduction for the peak at 7.18 eV present in the isolated thymine spectrum. Hence, for the most intense peak at 6.78 eV, the effect of
6.1 Excited states of DNA bases and their assemblies

HOMO  LUMO

Cyt  Gum

Thy  Ade

Figure 6.9: HOMO and LUMO Kohn-Sham wave functions of the GC<sub>H</sub> (top) and AT<sub>H</sub> (bottom) pairs. The cyan (magenta) isosurfaces represent positive (negative) charge values. Different atoms are indicated with different colors: carbon (green), nitrogen (blue), oxygen (red), hydrogen (white).

H-bonding is contrary to the hypochromicity described above for the GC<sub>H</sub> pair. In the out-of-plane spectrum (bottom right panel of Fig. 6.8), as for the GC<sub>H</sub> pair, we observe that the effect of hydrogen bonding is an overall blue-shift. In particular, the first peak (that has an \(n\pi^*\) character) is shifted by 0.4 eV; the second and fourth peaks are upward shifted by 0.2 eV and 0.3 eV respectively; the energy of the third peak is practically unchanged. In addition to the above features that originate from the individual base that enter each pair, new features appear in the spectra because the purine and the pyrimidine coexist in the Watson-Crick arrangement. This coexistence changes the nature of the frontier orbitals: The HOMO is purine-localized, the LUMO is pyrimidine-localized, and the value of the HOMO-LUMO gap is smaller than in the isolated bases. Consequently, peaks at lower energies emerge in the spectra: they are reported in Table VI, but the corresponding energy range is not shown in the figures, because the tiny oscillator strengths make them undiscernible from the more intense peaks. We also note that the extremely small intensity makes the quantitative assignment of these features less reliable than the others already discussed. In the case of GC<sub>H</sub>, we find excitation energies at 2.44 eV, 3.14 eV and 3.94 eV, with oscillator strengths of 0.001, 0.008 and 0.003. These
Chapter 6. Optical spectroscopy of biological chromophores

Oscillator strengths are two orders of magnitude smaller than the peak at 4.29 eV shown in the upper panel of Fig. 6.8. For the AT$_H$ pair, the lowest energy peak at 4.05 eV has an oscillator strength of 0.048. This transition has a small component also in the absorption for light polarized perpendicular to the base plane (see bottom right panel in Fig. 6.8). Its origin can be likely ascribed to charge transfer states, that have received particular attention from both experimental and theoretical viewpoints [Jortner 98]. However, we warn the reader that the identification of charge transfer transitions is to be taken with care at the current level of TDDFT when a local or gradient-corrected exchange-correlation functional is used [Dreuw 03, Dreuw 04, Gritsenko 04].

6.1.4 Stacked GC$_s$ and d(GC) structures

With the results reported in the previous section for the GC$_H$ pair, we can understand what happens in the optical absorption when a guanine and a cytosine dimerize through hydrogen bonding. Here, the GC$_s$ system is selected to check which effects arise when the same two bases dimerize in a different form, namely by stacking. Fig. 6.10 reports the averaged and direction-resolved spectra of the stacked GC$_s$ dimer. The comparison between Figs. 6.10 and 6.8 aims at disclosing the relative role of hydrogen-bonding and π-stacking in the optical response of nucleobase complexes. We also plot in Fig. 6.10 the linear combination of the spectra of the isolated constituent bases. Fig. 6.11 (top) illustrates the Kohn-Sham highest occupied and lowest unoccupied orbitals of the system. It is important to note that both the HOMO and the LUMO have charge density distributed around both the purine and the pyrimidine, at odds with the H-bonded GC$_H$ pair (compare Fig. 6.9, top) where the HOMO is centered at the purine and the LUMO at the pyrimidine.

As in the case of hydrogen-bonding, the shape of the spectrum it is not strongly altered, but important differences are encountered in the oscillator strengths. Looking at the first peaks at low energy, we see that the excitations due to the cytosine moieties are slightly blue-shifted (as for the GC$_H$ pair), while the guanine excitations appear not be affected. The resulting spectrum below 5 eV is made of two equally intense closely spaced peaks at 4.45 eV and 4.68 eV, whereas in the H-bonded GC$_H$ structure we observed two well separated peaks spaced by 0.4 eV and with different intensities. Hypochromicity is also observed in this low-energy range, whereas for the GC$_H$ pair hypochromicity occurs only in the high-energy range. In the range between 5 and 6 eV, we find an intensity enhancement of the weak peak at 5.31 eV and
6.1 Excited states of DNA bases and their assemblies

Figure 6.10: Photo-absorption cross section of the GC\textsubscript{s} stacked dimer (up) and of the d(GC) quartet (down). In each panel, the linear combination of the spectra of the two (up) and four (down) constituent bases is also shown. In the right panels the spectra resolved in the three spatial directions are shown.

A depression of the peak at 5.78 eV, which is present both in the isolated bases (guanine and cytosine) and in the H-bonded pair. In the high-energy spectral range, the dominant effect is the 39% hypochromicity for the main peak located at 6.15 eV: hypochromicity from $\pi$-stacking is thus enhanced with respect to hypochromicity from hydrogen-bonding (30%). Above the strongest peak, we find other less intense peaks at 6.47 eV, 6.87 eV, and 7.10 eV. Instead, in the H-bonded GC\textsubscript{H} pair, the high-energy range contains a peak at 6.78 eV with the same intensity as the peak at 6.17 eV, and then only an additional weaker one. The calculation of the GC\textsubscript{s} has been repeated for a geometry obtained by a slightly different relaxation scheme, in the DFT-PW91 framework [Calzolari 04a, Calzolari 04b]. This additional GC\textsubscript{s} geometry was considered just for a gross check of structural deformations induced by computational details. The starting configuration was fixed by taking guanine and cytosine from a previous DFT study of isolated bases [Di Felice 02] and putting them parallel to each other at an initial distance of 3.4 Å. The major difference
Chapter 6. Optical spectroscopy of biological chromophores

HOMO

LUMO

Figure 6.11: Isosurface plots of the HOMO and LUMO Kohn-Sham wave functions of the GC₈ π-stacked dimer (top) and of the d(GC) π-stacked quartet (bottom). The cyan (magenta) isosurfaces represent positive (negative) charge values. Different atoms are indicated with different colors: carbon (green), nitrogen (blue), oxygen (red), hydrogen (white).

PDB 400d+CHARMM+B3LYP  Ref. [Di Felice 02] + PW91

Figure 6.12: Two different conformations obtained for the π-staked GC₈ pair obtained by different structural relaxation schemes.

between the two GC₈ structures (Fig. 6.12) is the tilt angle, which is smaller in the PW91 relaxation. The two spectra are quite similar in both shape and intensity: minor differences are observed only in the first peak, that is shifted upward by 0.15 eV in the structure shown in the right panel of Fig. 6.12. The combined effects
of stacking and H-bonding on the absorption spectra are simultaneously present in Fig. 6.10 (lower panel), that corresponds to two stacked GC$_H$ pairs with the G’s on the same strand of the parent polymer [Gao 99]. The shape of the spectrum appears very similar to that of a single GC$_H$ pair (Fig. 6.8, top left), but the intensity of all peaks is reduced. Such decrease is a typical qualitative effect of the stacking arrangement, although the molecular details fix the quantitative aspects (we described the stacking between guanine and cytosine above, whereas we are now focusing on the stacking between two guanines). In fact, in the low-energy range we find again very slight shifts for the first two peaks, downward for the first and upward for the second, as in Fig. 6.8 (top left). However, the intensity of the second peak is equal to that obtained from the G+C combination, whereas in the single GC$_H$ pair it was higher. This is due to a depression of the second peak (guanine) induced by stacking. In the high-energy range, the hypochromicity due to both the $\pi$-stacking and the H-bonding couplings is confirmed. For the main peak located at 6.25 eV we find an intensity reduction by 62% with respect to the free monomers. The two kinds of base couplings seem to act separately and independently, in the sense that one does not affect the other: such separation was already reported concerning the electronic structure [Di Felice 02]. Summarizing this section, we have shown that stacked and H-bonded GC pairs present slight differences in the absorption spectra, both in the low-energy and high-energy ranges. Hypochromicity has been found in both configurations and results to be largest for the stacked pairs. Hypochromicity is very useful because this intensity change can be used to follow the melting of the secondary structure of nucleic acids when varying the temperature or environmental parameters.

**Conclusion**

In conclusion we presented a complete study of the optical absorption spectra of the five isolated gas-phase nucleobases and their assemblies: simple Watson-Crick pairs, simple $\pi$-stacking of two bases and more complex $\pi$-stacks Watson-Crick GC pairs. These calculations of isolated simple nucleobase-assemblies are a remarkable playground to prove the reliability of TDDFT for DNA-based materials. Remarkably, for the first time the optical properties were computed by an ab-initio method for a helical conformation of two stacked GC pairs, where H-bonding and $\pi$-stacking effects are active simultaneously and can be distinguished. The results can be summarized as follows.
i. For the isolated bases we get spectra in good agreement with previous theoretical works and (qualitatively) with experiments.

ii. We reproduce the proper ordering of the $\pi\pi^*$ excitations, namely that the excitation energy increases in going from C to G to A.

iii. The LUMO state has always a $\pi$-like character whereas the HOMO is $\pi$-like for the purines and $\sigma$-like for the pyrimidines.

iv. As concerns the base assemblies (Watson-Crick H-bond pairs and stacked configuration), we obtain that the shape of the spectrum is not much altered by the $\pi$-stacking or H-bond interactions. However, we always get hypochromicity in the high energy range of the spectrum. This hypochromicity is enhanced in the $\pi$-stacked case with respect the the H-bonded case.

v. For light polarized perpendicular to the bases we get a blue-shift of the spectra compared to the spectra of the isolated bases.

vi. In the stacked case, the HOMO and LUMO states are distributed both on the purine and pyrimidine bases, whereas in the H-bonded configuration the HOMO is in the purine and the LUMO in the pyrimidine (charge transfer-type excitation).

vii. When combining both H-bonding and $\pi$-stacking, the two effects add independently, and the hypochromicity in the UV is enhanced.

Anyway it is important to note that all our calculations are in the gas phase, which means that solvent and environment effects are not taken into account. This hinders a direct comparison with experimental data, as most of the available results correspond to nucleobases-assemblies in solution. However, several experimental and theoretical studies (including simplified models of the solvent) showed that the $\pi\pi^*$ transitions are only slightly affected by the presence of the solvent [Mennucci 01, Mishra 00, Shukla 02a]: precisely, they are insensitive to the polarity of the solvent, but may undergo red-shifts. On the contrary the “dark” $n\pi^*$ transitions turn out to be significantly sensible to the polarity of the solvent [Mennucci 01, Mishra 00, Fulscher 97, Shukla 02a, Shukla 02b]. As shown in Figs. 6.3-6.7, the absorption spectra of the DNA-bases is extremely anisotropic, due to their quasi-planar structure. Consequently, nearly all the oscillator strength is concentrated on the $\pi\pi^*$ transition (orders of magnitude more
intense than the $n\pi^*$ transitions). Those transitions are excited only for light polarized in the base plane. Therefore, the present results can be used to discriminate (albeit qualitatively) which features are mostly limited to the gas phase (those polarized out-of-plane) and which ones can be considered intrinsic to the DNA-complex. Furthermore, the role of charge-transfer states observed for instance in the AT$_H$ spectrum needs to be analyzed more in detail in order to understand their impact in the excited state dynamics of DNA-based complexes (note that those states are very likely to be dark, or with very low oscillator strength for light-induced electronic excitations). Besides the optical absorption results presented in this work, there is another optical technique that is widely used for the characterization of chiral biomolecules – circular dichroism. The technique used in the present work allows for a straightforward calculation of the rotatory power or circular dichroism spectra keeping the simplicity of the time-propagation scheme, i.e, without the need for empty states (see section (2.2.2) Eq.(2.34) and Ref. [Yabana 99b] for the details). The implementation and computation of circular dichroism spectra by TDDFT could in principle allow the identification of helical fingerprint in the optical characteristics, and more direct interpretation of standard post-synthesis experimental data. Work along this line is presently being done.  

\[ \text{1 D. Varsano, R. Di Felice, M. A. L. Marques and A. Rubio Unpublished} \]
6.2 The Green Fluorescent Protein (GFP)\footnote{This section is largely an adaptation of the article: M.A.L. Marques, X. Lopez, D. Varsano, A. Castro and A. Rubio: \textit{Time dependent density-functional approach for biological chromophore: the case of the green fluorescent protein}. Phys. Rev. Lett. \textbf{90} 258101 (2003). As such, the reported work includes collaboration of the rest of the authors of the article.}

The Green Fluorescent Protein (GFP) is a paradigmatic case of biological system where a biological process rely on the interplay between optical absorption of its photo-active center and its coupling to internal vibrational modes and to the environment (hosting protein). GFP is a protein produced by a jellyfish \textit{Aequorea} that lives in the North Pacific. Its peculiarity is that it is a bio-luminescent protein that absorb ultraviolet light and emits in the lower green portion of the visible spectrum. This molecule has become a unique tool in molecular biology due to its fluorescence and inertness when attached to other proteins\cite{Sullivan99} and has become a well established tool as a marker of gene expression and protein targeting in intact cells organism. GFP consists of 238 amino acids folded in a \(\beta\)-sheet barrel conformation. The barrel is a quasi perfect cylinder of 42 \(\text{Å}\) of height and 24 \(\text{Å}\) of diameter. In the interior of the \(\beta\) barrel there is the central helix and the chromophore. In Fig. 6.13 the secondary structure of the GFP (left panel) and the atomic structure of the chromophore (left panel) The chromophore is formed by Ser65, Tyr66 and Gly67. Ser65 is chemically modified, (its carbonyl carbon is linked to the nitrogen of Gly67 and the carbonyl oxygen is eliminated) such that the chromophore consists of two consecutive rings, the phenol-type ring of Tyr66 and a five membered heterocyle (imidazoline) formed by the backbone of Tyr66, the carbonyl carbon of Ser65 and the nitrogen of the backbone of Gly67. The tyroxyl hydroxyl group is part of a complex hydrogen bond network that depending on the environment favors its protonated (neutral) or deprotonated (anionic) form. The optical absorption spectrum of the wild type (wt)-GFP, measured at 1.6 K, shows two main resonances at 2.63 and 3.05 eV\cite{Creemers99,Creemers00} that are attributed to the two thermodynamically stable protonation states of the chromophore (negative and neutral configurations, respectively). The equilibrium between those two states can be controlled by external factors such as pH and by mutations that affect the chromophore environment\cite{Creemers99,Creemers00,Brejc97,Haupts98}. Nowadays there is an ample set of GFP-mutants with absorption and emission bands ranging from the violet to the red part of the spectrum. Excitation at either fre-
6.2 The Green Fluorescent Protein

Figure 6.13: Left: Cartoon of the crystal structure of GFP, taken from X-ray data ([Yang 96]). Right: AM1/MM optimized structure of the neutral chromophore inside the 1GFL protein. Some of the closest residues are also shown: His148, Arg96 (positively charged) and Glu222 (negatively charged). Different atoms are indicated with different colors: carbon (cyan), nitrogen (blue), oxygen (red), hydrogen (white). Green spheres correspond to the positions of the H-link atoms for the QM/MM procedure (see text).

frequency leads to fluorescent green-light emission, peaked at 2.44 eV, which is the main mechanism for energy release in wt-GFP. This internal photo-conversion process occurs very rapidly by excited-state proton transfer [Schwille 00, Cinelli 01] for the neutral chromophore. Only recently the optical absorption spectrum of the GFP anion chromophore was measured in vacuo [Nielsen 01]. It consists of a main peak at 2.59 eV in very close agreement with the peak assigned to the anionic configuration of the wt-GFP. It is clear that the photo-physics of the GFP is governed by a complex equilibrium between the neutral and anionic configurations. The relevance of other proposed configurations, namely of the cationic and the zwitterionic, has been ruled out [Weber 99, Yoo 01, Tozzini 01]. Several calculations of the excited states have been performed using ab-initio quantum-chemistry methods [Weber 99, Yoo 01, Tozzini 01, Helms 00]. Unfortunately, these calculations yielded optical absorption spectra in very poor agreement with experiment. A microscopic model account-
ing for the optical properties of the GFP chromophore including its blinking and photo-bleaching dynamics is still missing [Schwille 00, Cinelli 01]. In the present work we prove that a combination of a quantum-mechanics/molecular mechanics method (QM/MM) to obtain the structural properties and time-dependent density functional theory (TDDFT) to treat the electronic excitations provides a very good description of the optical properties of the GFP \textit{in vacuo}. In the following section we shortly describe the the QM/MM method used to obtain the structure of the chromophore and we give the technical details of the calculation, while in section (6.2.2) we give the obtained results.

6.2.1 Computational Framework

Biological systems, such as proteins, nucleic acids etc. are constituted for a big number of atoms, so that turns to be computationally impossible to perform a complete quantum mechanical description with the methods described above. Nevertheless, in many situations only a small part of the whole system, the chromophore, is the responsible of the UV optical absorption of the system, so we can resort to the TDDFT limiting the calculation to the subsystem of interest. Anyway, as mentioned before, the starting point for a TDDFT calculation is the ground state wave function usually calculated via standard DFT schemes that of course requires the knowledge of the structure of the system. So, even if we are interested in only a small portion of the system, in order to have a correct description of its structure, turns to be important to consider all the whole system because the interaction between the chromophore and the near atoms could play an important role in its structural properties. To take into account such interactions a viable method is the hybrid technique called QM/MM (Quantum Mechanics Molecular Mechanics) [Brunger 88, Laio 02]. Such method is an approximate technique that permit to treat the reacting center of a big molecule with Quantum mechanical method, whereas the remaining part is treated in classical way via empirical potential (See left part of Fig.(6.14)). In the QM/MM framework the Hamiltonian of the system is given by the sum of the terms representing the QM region, the MM region and the interaction between them:

\begin{equation}
\hat{H}_{\text{eff}} = \hat{H}_{\text{QM/QM}} + \hat{H}_{\text{MM/MM}} + \hat{H}_{\text{QM/MM}}
\end{equation}

\hat{H}_{\text{QM/QM}} \text{ is the Hamiltonian describing the nuclei and electrons in the quantum region, such term can be solved using different quantum methods as DFT, Hartree Fock or semi-empirical methods.}
**Figure 6.14:** Left: Scheme of the division of the system in the QM/MM framework. Right: Schematic picture of the border between the classical and quantum part of the system.

\( \hat{H}_{\text{MM/MM}} \) is a molecular mechanics Hamiltonian, the atoms are treated classically and it depends only on the atoms position. The entire region is treated with force fields. The force fields describe either the interaction among bonded atoms depending on the stretching, bending and the torsion of the bond, either the electrostatic and Van der Waals interaction among the non-bonded atoms.

\( \hat{H}_{\text{QM/MM}} \) describes the interaction between the classical and quantum regions and can be decomposed as:

\[
\hat{H}_{\text{QM/MM}} = \hat{H}_{\text{QM/MM}}^{\text{elec}} + \hat{H}_{\text{QM/MM}}^{\text{vdW}} + \hat{H}_{\text{QM/MM}}^{\text{bonded}}
\]

The first term take into account the electrostatic interaction between the electrons and nuclei of the quantum region with the classical part, in this treatment the atoms of the classical part are treated as external point charges. The second term describe the Van Der Waals interaction between the QM atoms and MM atoms and finally the third term represent the interaction at the border. This term is introduced when the border is inside a molecule and contains the classical field terms of the MM atoms bonded to QM atoms. In many situation the border pass through a covalent bond. There exist different technique to model such bond when it is a single bond [Reuter 00], while to treat multiple bonds turns to be problematic due to their sensibility to polarizability effects. In this work we have used the method called link-atom. In this method each time that the border pass through a bond the QM and MM part are connected via an hydrogen atom (see right part of Fig.6.14). The ‘artificial’ hydrogen atom is included in the quantum region, but does not interact in electrostatic way with the classical region, furthermore this H-atom is forced to be aligned in the direction of the bond of the border during the relaxation of the system.
The structures

The GFP structures were prepared according to the following protocol. The X-ray structure (1.9 Å resolution) of the GFP from Ref.[Yang 96] (PDB code: 1GFL) illustrated in the left panel of Fig 6.13 was taken as the reference structure. In the X-ray structure, several water positions were identified. In the preparation of the structures, we only kept the water molecules that lied within 6 Å of the chromophore. All other crystallographic water molecules were deleted. The position of the hydrogens were initially obtained using the HBUILD command [Brunger 88] of CHARMM [Brooks 83, MacKerrel 98]. In order to relax the geometry of the system 3 consecutive optimizations were carried out. An initial optimization was performed with all backbone and chromophore atoms fixed at their crystallographic positions. Non-bonded interactions were treated using a spherical cutoff of 12 Å with an atom-based potential shift method for the van der Waals terms and the force-shift method for the electrostatic terms. The system was minimized using the steepest descent and adaptive basis Newton-Raphson minimization algorithms [Brooks 83, MacKerrel 98]. In a second step we allowed relaxation only of the coordinates of the chromophore. As the GFP chromophore (specially the imidazoline heterocycle) does not correspond to the typical structure adopted by serine, tyrosine or glycine, there is a lack of specific force field parameters. Therefore, we performed this step within a QM/MM hybrid method [Field 90], using the AM1 semi-empirical Hamiltonian [Dewar 95] to describe the quantum subsystem. The QM region was defined by three amino-acids, Ser65, Tyr66 and Gly67, and the frontier between QM and MM regions was treated within the H-link approximation. In this approach a H atom is included whenever the frontier between the QM and MM regions passes through a chemical bond. This H-link atom is forced during the minimization to be aligned with the frontier bond, and does not interact with the MM atoms. In order to avoid the QM/MM frontier to be in the C(O)-N peptide bond the carbonyl group of Gly67 was removed from the QM subsystem and the carbonyl group of i Phe64 was included. In this way, the two H-link atoms cut through C-C bonds. Finally, from this geometry we performed a full relaxation allowing the chromophore and every protein atom within 10 Å of the chromophore to relax. The final structure of the chromophore with the most important neighbors residues is depicted in the right panel of Fig. 6.13. We checked the minimization, by computing the forces on the final geometry using a DFT scheme for the quantum part of the QM/MM Hamiltonian [Marques 03a]. The anionic form of the chromophore was prepared
from deprotonation of the Tyr66 and protonation of Glu222. The proton transfer is mediated through a water molecule and Ser205. The water molecule, depicted in Fig. 6.13 (right panel), receives a proton from Tyr66 and donates a proton to Ser205, which in turn donates its original proton to Glu222. As a result, Glu222 is neutralized. The role of the protein backbone is important for the structural relaxation of the anionic form. The main structural difference to the neutral form is the relative orientation of the Tyr66-ring with respect to the imidazoline heterocycle: In the neutral form the two ring planes are found to be slightly displaced from planarity, the $C_\alpha-C_\beta-C_7-C_8$ dihedral being $-10.9^\circ$. In the anionic form the co-planarity of the two rings is enhanced, through the reduction of the $C_\alpha-C_\beta-C_7-C_8$ dihedral to $-1.8^\circ$. Concerning bond distances, the largest change upon deprotonation of Tyr66 corresponds to the shrinking of the C-O(H) bond distance from 1.38 Å in the neutral form to 1.28 Å in the anionic form. From these relaxed structures, we extracted the quantum-mechanical subsystems, that we subsequently used for our TDDFT calculations.

**The absorption spectra**

The absorption spectra of the chromophore has been calculated in the same framework of the DNA basis described in the previous section. The electron-ion interaction is described through norm-conserving pseudo-potentials [Troullier 91, Kleiman 82], and exchange-correlation effects we treated within the local-density approximation [Ceperley 80]. We stress that in the present study the specific form of the exchange-correlation functional should not introduce major modifications [Marques 01]. This is, however, untrue for studies of charge-transfer processes and isomerization mechanisms.

**6.2.2 Results**

The computed spectra of the neutral and anionic conformations of the GFP chromophore are given in Fig. 6.15, together with the experimental spectrum of the wt-GFP. The spectra are averaged over the three spatial directions. Light polarized along the “x”-direction is responsible for the lowest optical transition (see the inset of Fig. 6.15), and corresponds to a $\pi-\pi^*$ transition between the HOMO and LUMO orbitals of both neutral and anionic forms. The molecule is nearly transparent to visible light polarized along the other two orthogonal directions. GFP
turns out to be a rather anisotropic molecule in the visible, property that can be used to enhance the photo-dynamical processes in well oriented GFP samples for opto-electronic devices. The differences between the LUMO and HOMO eigenvalues, sometimes taken as a estimate for the HOMO-LUMO excitation energy, are respectively 2.19 and 1.61 eV, for the neutral and anionic structures. It is common practice to use these values as estimations of the physical excitations. This leads, in the case of the GFP, to a very bad agreement with experiment. However, in TDDFT the difference of one-particle eigenvalues is renormalized by the Coulomb and exchange-correlation terms\cite{Fiolhais 03, Onida 02}. Once these effects are included, the main excitation peaks for the neutral and anionic forms move to 3.01 and 2.67 eV respectively. These values are now in really good agreement with the measured excitation energies, located at 3.05 and 2.63\cite{Creemers 99, Creemers 00}. The $\pi$-$\pi^*$ excitations are no longer pure HOMO-LUMO transitions and include contributions from virtual particle-hole excitations involving several occupied and unoccupied states. Some of the most relevant states are depicted in Fig. 6.16. The oscillator strength of the $\pi$-$\pi^*$ transition is larger in the anionic than in the neutral GFP. It is, however, possible to obtain a quantitative description of the spectra of the wt-GFP by assuming a $\sim$ 4:1 ratio for the concentration of the neutral/anionic forms. This ratio is very close to the estimated experimental ratio of 80% neutral and 20% anionic\cite{Sullivan 99}. The measured peaks can be clearly assigned to either the neutral or anionic forms of the GFP. The suggested three-state model of the wt-GFP photo-physics contains the two thermodynamically stable neutral and anionic configurations, and an unstable intermediate state that apparently corresponds to the anionic chromophore in a non-equilibrium protein environment\cite{Brejc 97}. Other intermediate state relaxation processes through cis-trans isomerization and a new protonated zwitterionic form have also been proposed\cite{Weber 99}. Our calculations give further support to the predominance of the neutral and anionic forms in wt-GFP in agreement with the analysis of the infrared spectra\cite{Yoo 01, Tozzini 01}. This sustains the proposed proton shuttle mechanism between the protonated and de-protonated forms of the chromophore, through the corresponding charged states of the Glu222 residue where the proton-shuttle ends. Furthermore, the structural differences between the two anionic structures is very small, and changes the main absorption peak by $\sim$0.1 eV, which is of the same order as the precision of our calculations. The cationic conformation is derived from the neutral form by protonation on the imidazoline nitrogen that is formally double bonded to a carbon in the neutral state. Its spectrum consist of a major peak at 2.8 eV in relative agreement with the measured value for
6.2 The Green Fluorescent Protein

![Graph of photo-absorption cross-section vs energy](image)

**Figure 6.15:** The computed photo-absorption cross-section, $\sigma$, compared to the experimental measurement. The dashed line corresponds to the neutral chromophore, the dotted line to the anionic, whereas the green and blue curves are the experimental results of Ref. [Nielsen 01] and Ref. [Creemers 99, Creemers 00] respectively. For comparative purposes, we divided the anionic results by 4 with respect to the neutral results. Inset: decomposition of the computed spectra of the neutral species in the three directions, showing the inherent anisotropy of the GFP molecule.

A model chromophore in aqueous solution, $3.15\text{eV}$ [Bell 00]. This predictive power can prompt the use of TDDFT combined with time-resolved optical spectroscopy to map the concentration of the different GFP forms in solution upon excitation, and extract information on the isomerization paths and lifetimes of the initial and transition states. The fact that the computed absorption spectra of the isolated chromophore is in close agreement with the measured spectra points to an efficient electrostatic shielding of the chromophore by the rigid $\beta$-barrel. This justifies the comparison between *in vacuo* and *in vivo* spectra [Nielsen 01]. In spite of the rigidity of the $\beta$-barrel, there is a change in the neutral/anionic concentration ratio with temperature, glycerol content of the solution, and external pH [Sullivan 99]. This fact can be understood by considering that the Tyr66 hydroxyl points toward the protein surface and it is H-bonded to a water molecule, are therefore sensitive to bulk proton concentrations. In particular the raise of the anionic population as the pH is increased can be understood in terms of the protonation of Glu222 residue. In fact, replacing the Ser65 by several mutants can lead to the suppression of the anionic
Figure 6.16: Kohn-Sham states of the neutral (left) and anionic (right) GFP chromophores. The red (blue) isosurfaces represent positive (negative) charge values.

peak in the spectra, through a change in the H-network that prevents ionization of the Glu222 [Brejc 97]. Similarly, a reduction of the pH leads to a drop of the neutral peak and consequent enhancement of the of the anionic peak [Haupts 98]. This neutralization triggers the conversion from neutral to anionic isomers in solution. In the same way, our calculations show that the excitation leads to a slight charge transfer from the phenolic to the imidazoline ring (mainly at the bridging group as already observed in previous calculations[Helms 00]). We observed that the main effect of the excitation in the structure is to increase the strength of the single bonds and weaken the double bonds. This has important consequences for the proton affinity of the different sites. Clearly, after the $\pi-\pi^*$ transition in both neutral and anionic forms, the imidazolinic N increases its proton affinity. There is also a reduction of the charge in the phenolic O atom of the Tyr66 after excitation of the neutral GFP that may trigger the deprotonation. In conclusion, we have shown that a combined
QM/MM and TDDFT approach is able to reproduce the optical response of the GFP. This is a major step toward the first-principles description of excited-state dynamic of important biological photo-receptors. Transient and time-resolved optical spectroscopy could be studied. However, in spite of the good agreement, some questions remain open. For example, how does the excitation in the GFP trigger the proton shuttle mechanism and what is the time-scale for this process? To answer these questions we have to go beyond the present work where only the QM subsystem was considered to obtain the optical response. The proton-transfer involves structural modifications of the environment that have to be properly described by a modified QM/MM approach. For this, the standard QM/MM methods have to be generalized to cope with excited state dynamics, and eventually to include the possibility of charge transfer between the QM to the MM parts.

\[1\] Similar good agreement has been obtained for other mutants of the GFP chromophore, in particular the blue fluorescent protein [Lopez 05]
The application showed in the previous chapters have shown that TDDFT is a fast and reliable tool for the description of excited states for different class of finite systems. In particular we have seen in sections (6.1 and 6.2) the good performance of the method for the studied biological systems, and in general as asserted above it has be shown to give results in quite good agreement for a variety of nanostructured materials[7]. Moreover we will show in chapter 8 how TDDFT can be used as a tool for the study of systems under the influence of strong laser fields, in particular for the study of photo-electron spectroscopy problems. In this chapter, on the other hand, we concentrate on a paradigmatic case in which TDDFT, when applied with standard exchange-correlation functionals (ALDA or AGGA), fails dramatically. The optical absorption of long quasi one-dimensional molecular chains, calculated with local density approximation or gradient corrected functionals, gives wrong results and the static axial polarizability and hyper-polarizability of long chains are overestimated by orders of magnitudes when compared with experiments and calculation of quantum chemistry as configuration interaction methods. As stated in section (2.1), TDDFT is an exact reformulation of the many body Schrödinger equation, so the failure of the theory, for this class of systems, has to be attributed to the approximation made in practical applications: i.e. the exchange-correlation (xc) potential used for the ground state calculation, and the time-dependent xc-potential/kernel used for the excited state calculation. This failure is related to the so-called ultra non-locality problem, discussed in section (1.2.2), i.e. to the strong non-local dependence of the exchange-correlation potential when an electric field is applied [van Gisbergen 99, Gritsenko 01]. The reason of the failure of the ALDA is indeed its spatial locality in the xc kernel. Since the LDA depends explicite on

\[\text{This section is largely an adaptation of the article: D. Varsano, A. Marini and A. Rubio: Excitonic properties of quasi 1D systems: from finite chains to infinite polymers to be published. As such, the reported work includes collaboration of the rest of the authors of the article.}\]
Chapter 7. Optical absorption of quasi 1D systems

Figure 7.1: Left: Axial polarizability per oligomer of polyacetylene calculated in ALDA and VK [van Faassen 02], Hartree Fock [Kirtman 95] and MP2 [Toto 95] approximations. Right: The same quantities calculated for H2 hydrogen, compared with coupled Hartree Fock, MP4 and coupled cluster CCSD(T) [Champagne 95a] methods. Figures adapted from Ref.[van Faassen 02].

the density, the ALDA kernel at the center of the molecule will be insensitive to the variation of the density at the end-side of the chain induced by the electric field, while for the exact exchange correlation potential this end side charge contributes to the counteracting electric field described in section (1.2.2) that increase linearly along all the chain. In Fig. 7.1, adapted from Ref.[van Faassen 02] it is illustrated how wrong the LDA behaves for the axial static polarizability of two systems, the polyacetylene and an $H_{2n}$ chain, as a function of the polymer length. We observe that the error of the ALDA increase with the length of the polymer when compared with accurate MP2 calculation, for polyacetylene and MP4 calculation for the hydrogen chain. A way to take into account the macroscopic polarization is by using information coming from the induced current density rather than the density, as in principle it is easy to mimic those effects with local functional of the current whereas they should be extremely non local for functionals of the density. M. van Faassen et al.[van Faassen 02] studied the axial polarizability of different polymers solving the response equations within the Time Dependent Current Density Functional Theory (TDCDFT), using a current-response kernel proposed by Vignale and Kohn (VK-kernel) [Vignale 96]. These results, are shown in Fig.7.1, labeled as VK. We see that this approach gives very good results for the polyacetylene , and in general for
\( \pi \)-conjugated systems\cite{van Faassen 03}. However in the right panel of the figure we observe that in the case of the \( H_{2n} \) chain, where the dominant contribution of the induced current comes from the polarized \( \sigma \) bonds, this method gives only a small improvement with respect the ALDA result. A correct behavior of the xc electric field and consequently a correct behavior of the static polarizability is given by orbital dependence functionals, in particular the simple one based on an exact exchange treatment.\(^1\) Sanchez \textit{et al.} \cite{Sanchez 03} obtained very good results for polyethylene, polythiophene and the hydrogen chains. In order to get the correct behavior of the polarizability one has to solve the cumbersome OEP equation (1.25), because approximation to this equation as the KLI \cite{Krieger 92} and the CEDA \cite{Gruning 02} partially correct the local density (LDA) and gradient corrected (GGA) approximations, but polarizabilities are still significantly larger than Hartree Fock and EXX \cite{Kümmel 04, Gruning 02}. However we mention that for infinite systems, empirical cutoffs are introduced to construct the \( f_{xc} \) in exact exchange \cite{Kim 02a, Kim 02b}, that somehow account for the screening of the electron-hole interaction. Therefore it is important to address the issue of including screening consistently. This is the goal of the present chapter. We study these two system, the polyacetylene as prototype of a \( \pi \)-conjugated system and the model \( H_{2n} \) chain in the TDDFT framework using the new developed frequency-dependent non-local \( f_{xc} \) kernel described in section (3.5). We look at the optical properties of finite chains in function of the length in both MBPT and TDDFT with this new kernel. We also address the limit of infinite chains. In practise all these systems are studied using a plane wave basis set with the supercell approximation with the truncated Coulomb potential described in chapter 5. In particular to avoid spurious cell-cell interactions we cut the coulomb potential outside a sphere Eq. (5.11) for the single monomers calculation, outside a finite cylinder Eq. (5.32) for the finite chain systems and outside an infinite cylinder Eq. (5.12) for the infinite polymers. This chapter is organized as follows: In section (7.1) we will describe the studied systems, i.e. the trans-polyacetylene polymer and the chain of \( H_2 \) molecules. In section (7.2) we will analyse the performance of the new kernel described in section (3.5) when applied to a finite system. The optical properties of the finite chains in function of the length of the system are discussed in section (7.3), and finally section (7.4) reports the results obtained for the 1D periodic systems, i.e. the infinite polymers.

\(^1\) The good performance of this scheme is also exhibited by a HF calculation. This is not true for polyacetylene where correlation is also important.
7.1 Description of the systems

As mentioned above, the two systems studied in this work are the trans-polyacetylene chain and a molecular chain of hydrogen atoms. Trans-polyacetylene is the simplest conjugated polymer, and during the last two decades this class of systems have become an important field of research for its electronic and optical properties [Heeger 88]. For this reason it is an ideal candidate for studying the role of electron-hole correlation and the performance of the new kernel described in section (3.5) for low-dimensional systems. Polyacetylene has a planar structure and presents alternating single double bonding between carbon atoms. We used the geometry taken from by optimization at Hartree Fock level [Kirtman 95] as done in Ref. [van Faassen 02] for comparative purpose. The structure is sketched in the top panel of Fig. 7.1. The difference in length between carbon single bonds and double bonds is an important structural parameter and turns to be very similar to NMR and X-ray experiments [Yannoni 83, Zhu 92]. For the calculation of finite chain we have added hydrogen atoms along the direction of the C-H bond as illustrated in the inset of Fig.7.3 for one monomer. The second system we have studied is a model molecular hydrogen chain. This model, in the past, has been used to explain different features of real systems ([Liegner 85] and reference therein), indeed increasing the bond length alternation of the polymeric hydrogen chain this model provides a continuous description for a transition between a normal metallic one-dimensional chain to the Peierls distorted semiconductor and insulator. For this reason it turns to be an ideal system to investigate the effect of electron correlation on the longitudinal polarizability of increasingly large system. Among the different length in bond alternation we have choose the struc-
ture sketched in the bottom panel of Fig. 7.1. The hydrogen atoms have an intra-molecular distance of 2 \( \text{a.u.} \) and the inter-molecular distance between \( H_2 \) molecules is 2.5 \( \text{a.u.} \). Sanchez et al. [Sanchez 03] showed that this is the geometry where the LDA polarizability has the maximum error with respect the Hartree Fock calculation for two interacting \( H_2 \) molecules \(^2\), so it constitutes a stringent test case for the new \( f_x^{(1)} \) introduced in section (3.5). In all the calculation the position of the atoms are kept fixed. The ground state wave functions and eigen-energies of all the studied systems have been performed with the plane wave ABINIT code in DFT framework using the LDA approximation in the Teter Pade parametrization [Goedecker 96], if not differently specified. The electron-ion interaction has been considered via Troulliers-Martin pseudopotentials [Troullier 91]. The optical properties have been calculated with the code SELF as described in section (4.3).

The longitudinal polarizability per monomer of this model with different bond alternation has been studied with different techniques and approximations as coupled and unrestricted Hartree Fock, Møller Plesset [Champagne 95a, Champagne 95b], DFT [van Faassen 02, Sanchez 03, Kümmel 04, Baer 05], and quantum Monte-carlo [Umari 05].

### 7.2 One Monomer spectra

The first systems we have considered are single oligomers of the atomic chains: an isolate monomer of polyacetylene and an \( H_2 \) molecule (look insets in Fig 7.3). For these small systems we have compared the TDDFT results when the new non-local and energy dependent kernel described in section (3.5) is used, with the absorption spectra obtained solving the BS equation of MBPT. The results in different approximations are shown in Fig. 7.3. For both molecules we have used a cubic supercell of side length of 25 \( \text{a.u.} \) for \( H_2 \) and 33 \( \text{a.u.} \) for the polyacetylene monomer. To avoid the spurious interaction of the supercell images we have used a cutoff coulomb potential of spherical shape Eq. (5.11). The first step for both BS and TDDFT calculation is the evaluation of the quasiparticle energies that has been calculated

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\(^2\) This paper they attributes the failure of the LDA to the self-interaction error: for small inter-molecular distances, as a covalent bond, the system does not have fractional number of electrons, therefore the error is small, when the inter-molecular distance increase the applied electric field produces charge transfer and the error increases, then for larger inter-molecular distances the system approach two independent \( H_2 \) molecules, the charge transfer decreases and consequently the LDA error.
Figure 7.3: Calculated absorption spectrum for the polyacetylene monomer (top panel) and the hydrogen molecule (bottom panel). The BS (TDDFT) solutions in different approximations are depicted with solid (dashed) lines, see main text for a discussion. The yellow line is the independent quasiparticle spectrum in the GW approximation. In the inset we show the structures indicating carbon (hydrogen) atoms in green (blue).
in the GW approximation, and we find an HOMO-LUMO gap of 12.44 eV for the polyacetylene and 15.60 eV for the \( H_2 \) molecule, while the LDA gap is respectively of 5.63 eV and 8.01 eV, so the quasiparticle correction is very important, about 100% \(^3\). The independent quasiparticle spectra is shown in Fig. 7.3 with yellow solid line. When the electron-hole interaction is taken into account clearly the spectrum is shifted to lower energies. The BS solution when only the resonant part of the excitonic Hamiltonian is taken into account is depicted with black line. The agreement of the BS equation and the first order resonant \( f^{(1)}_{xc} \) of TDDFT (blued dashed line) Eq. (3.54) is almost perfect for the two systems \(^4\). Despite the good agreement between the two resonant calculation we note that when a causal \( f^{(1)}_{xc} \) kernel is constructed the absorption spectrum (purple dashed line) shift to lower energy of about 1.2 eV for the polyacetylene and 1 eV for the \( H_2 \) molecule. Such discrepancy between the resonant and causal response in the TDDFT has its origin in the fact that in the causal solution of the TDDFT equation we have mixed \( \{vc\} \) and \( \{cv\} \) pairs. Therefore it is clear that we have to go beyond the resonant solution of the BS equation and including the coupling terms in the excitonic Hamiltonian (see section (4.3)). We have done this and the results obtained by diagonalizing the full excitonic Hamiltonian Eq. (3.43) (red solid line in Fig. 7.3) is in fact shifted to lower energy. So we see that the resonant approximation, extensively used for bulk calculations, for the studied 0D systems it is not valid anymore, and the coupling part plays an important role. We can see now that the agreement between the BS and TDDFT calculation it is not so good as for the resonant part only. The dif-

\(^3\) The GW calculation has been performed as described in section (4.3), calculating the dielectric function within the plasmon pole approximation Eq. (4.18). In the exchange part of the Self Energy Eq. (4.16) we have used all the G vector used to describe the ground state KS wave functions, that correspond respectively to an energy cutoff of 36 Ry for polyacetylene and 40 Ry for \( H_2 \). For the correlation part of the Self-energy, Eq. (4.17), we have considered a number of KS states up to 25 eV (23 eV) for polyacetylene \( (H_2) \) in the occupied-unoccupied energy difference, and a cutoff in the plane waves of 5 Ry (6 Ry).

\(^4\) In order to get converged results in the BS Hamiltonian, electron-hole Kohn Sham pairs has been considered up to 27 eV (23.5 eV) for the polyacetylene oligomer (hydrogen molecule), the same number of bands has been included for the construction of the response function used in the screening. In the exchange part of the BS equation (Local field in TDDFT) have been included respectively plane waves up to 10 Ry for the polyacetylene and 12 Ry for \( H_2 \), while for the construction of the dielectric function in the direct term we used a cutoff of 2.2 Ry for the polyacetylene and 2.5 Ry for the hydrogen chain. For the construction of the TDDFT kernel \( f^{(1)}_{xc} \) a threshold of \( 10^{-9} \) has been used in the SVD routine, and only 81 G-vectors (0.5 Ry) are needed to get converged results.
ference between the two absorption spectra is due to the contribution of the direct term in the coupling part. This can be seen from the fact that the \( f^{(1)}_{xc} \) kernel is constructed starting from the only resonant part of the kernel of the BS equation, and while the exchange part of the coupling is recovered in the TDDFT equation when causal response function are considered, including the local field effects, the direct part in the coupling is neglected. This is shown in the spectra plotted in green in Figure 7.3 labeled [only \( K^x \) in cpl] where we have diagonalized the BS equation including the resonant part of Eq. (3.44), and only the exchange part in the coupling Eq. (3.46). In this case agreement is restored. Anyway, fortunately the contributions that are included in the \( f^{(1)}_{xc} \) (the direct term in the coupling part) plays a minor role. The overall difference between the full BS equation and the TDDFT causal calculation is about 0.2 eV. For the sake of clarity we have not reproduced in the top of Fig. 7.3 the ALDA spectrum, showed before in Fig. 5.10, but as expected for finite systems, in the case of just one isolate molecule, also the ALDA reproduce well the absorption spectrum (compared to the BS result). In conclusion, we have shown that TDDFT with a first order \( f^{(1)}_{xc} \), that were previously tested for bulk and surface systems [Marini 03, Sottile 03, Pulci 06], reproduces fairly well the optical properties of isolated 0D systems. Minor discrepancies are found due to the absence of the contribution coming from the direct term in the coupling part of the BS Hamiltonian in the kernel, that in some cases can play a role. Anyway, as we will see in the next section, the contribution of the coupling part in the absorption spectrum get smaller as the length of the polymeric chain is increased, and consequently the discrepancies observed here tends to disappear in the long chain limit, where the ALDA fails for the reason illustrated in the introduction.

### 7.3 Optical properties of finite chains

In the last section we have seen the performance of the new kernel \( f^{(1)}_{xc} \) at first order when applied for studying small isolated molecules and we have found satisfactory results when compared with the ALDA calculation and Bethe Salpeter calculation. Now in this section we study the optical properties of the \( \text{trans} \)-polyacetylene polymer and the \( H_{2n} \) chain in function of the length of the chain\(^5\). As stated in the

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\(^5\) For all these calculation, apart for the single monomer where we have used cubic supercells, we have used parallelepiped supercells with sides of 25 \( \text{a.u.} \) in the directions orthogonal to the chain axis for the hydrogen and 30 \( \text{a.u.} \) for the polyacetylene. In order to avoid spurious interactions between cells we have used the cutoff coulomb interaction described in chapter (5) with a cylin-
7.3 Optical properties of finite chains

<table>
<thead>
<tr>
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<th>HOMO-LUMO Energy Gap</th>
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<tr>
<td></td>
<td># $H_2$ units</td>
</tr>
<tr>
<td>1</td>
<td>8.01</td>
</tr>
<tr>
<td>2</td>
<td>5.93</td>
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<tr>
<td>3</td>
<td>4.86</td>
</tr>
<tr>
<td>5</td>
<td>3.81</td>
</tr>
<tr>
<td>7</td>
<td>3.31</td>
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</tbody>
</table>

**Table 7.1:** Calculated HOMO-LUMO Energy gaps in eV, for finite $H_{2n}$ chains in function of the number of the $H_2$ units within the LDA and GW approximation.

introduction we know that for this class of system the ALDA it is note anymore a good approximation. We have considered the polyacetylene polymer up to four monomers ($C_8H_{16}$) and the hydrogen chain up to seven $H_2$ units. The first step of our calculation is the evaluation of the quasi-particle energy levels for all the studied systems, needed for both the BS and the TDDFT calculation with the $f_{xc}^{(1)}$ kernel. The calculated HOMO-LUMO energies both in LDA and GW approximation for the Hydrogen chain are reported in Tab. 7.1. The HOMO-LUMO energy gaps in both LDA and GW scales with the number of monomers units ($N$), following the empirical relationship $1/N$, that holds for short oligomers as observed in Ref. [Hutchinson 03] for a large class of polymers. Next we have calculated the optical absorption of the chains adding additional monomer units both in BS framework and in TDDFT with the non-local and energy dependent kernel $f_{xc}^{(1)}$. The effect of the coupling term in the solution of the BS equation is analyzed in the top panel of Fig. 7.4 where we compare the binding energy of the bright excited state for each system calculated with a resonant and a full BS calculation. The binding energy is calculated as the energy difference between the excitonic peak and the QP gap. From those results we observe that the contribution of the coupling term to the absorption spectra reduces systematically with the length of the chain, in particular the position of the absorption peak calculated with the resonant approximation for the case of seven $H_2$ differs by less than 0.15 eV from that calculated diagonalizing the full Hamiltonian. In the bottom panel of Fig. 7.4 we plot the calculated absorption spectra of the chains both in the BS framework and in TDDFT with the $f_{xc}^{(1)}$ kernel. We observe that due to the minor effect of the coupling term in the absorption spec-

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drical shape along the chain axis with a finite height, (see Eq. (5.32)), as in Ref. [Spataru 04a], and a radius of 9 a.u for the hydrogen chains and 12 a.u. for the polyacetylene.
Chapter 7. Optical absorption of quasi 1D systems

Figure 7.4: top: Calculated binding energies for the active excited states of a finite $H_{2n}$ chain in function of $H_2$ units. The dots (squares) refers to include (neglect) the coupling term in the excitonic matrix Eq. (3.43). The arrow indicates the bulk limit value. Bottom: Calculated BS (solid line) and TDDFT (dashed line) absorption spectra of the $H_{2n}$ chains.
7.3 Optical properties of finite chains

Figure 7.5: Excitation energies for the singlet and triplet excited states of the chains. With bullets (triangles) we indicate the singlet (triplet) excitations. In red (blue) are indicated the singlet (triplet) excitations with oscillator strength different from zero. The agreement between the two calculation improves with chain length, and for the larger chains studied here the results obtained with the two methods are quite indistinguishable. In Figure 7.5 are plotted the whole excitation energies of the optically active singlet states (bullets) in function of the number of monomers units up to 13 eV, together with the triplet excited states obtained by diagonalization of Eq. (3.47) (triangles). The bright excitations are indicated with colored symbols, while in black we indicate the excitations with zero or very small oscillator strength. The same study has been made for the polyacetylene chain up to four monomer. The calculated LDA and GW HOMO-LUMO gap energies are reported in Tab. 7.2, and the $1/N$ behavior encountered for the $H_{2n}$ chain

<table>
<thead>
<tr>
<th># monomer units</th>
<th>LDA</th>
<th>GW</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>5.63</td>
<td>12.44</td>
</tr>
<tr>
<td>2</td>
<td>3.94</td>
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<td>7.94</td>
</tr>
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<td>4</td>
<td>2.44</td>
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</tr>
</tbody>
</table>

Table 7.2: Calculated HOMO-LUMO Energy gaps in eV, for finite trans-polyacetylene chains in function of $(C_2H_4)$ units within the LDA and GW approximation.
Chapter 7. Optical absorption of quasi 1D systems

Figure 7.6: Top: Calculated BS absorption spectra for the finite chain of trans-polyacetylene in function of the monomers units (solid lines). The TDDFT spectra with the $f_{xc}^{(1)}$ kernel introduced in section (3.5) are shown with dashed lines. In the inset we show the singlet and triplet calculated excitation energies, together with experimental results. Experimental absorption spectra Exp1 and Exp2 are from Ref. [Granville 81]. With arrows we indicate the bulk limit values. Bottom: Excitation energies for the singlet and triplet excited states of the chains. With bullets (triangles) we indicate the singlet (triplet) excitations. In red (blue) are indicated the singlet (triplet) excitations with oscillator strength different from zero.
is also obtained for the polyacetylene chain. The calculated absorption spectra are plotted in Fig. 7.6. The agreement between the BS and TDDFT calculations is worse than in the case of the hydrogen chains for the single oligomer and for the two monomers chain, but as in the case of the hydrogen chain we found that the agreement improves for larger chains, when the coupling contribution to the spectra can be neglected. For the three and four units chain we found a quite perfect agreement between the BS calculation and the TDDFT calculation. In the inset of the same figure we plot the singlet and triplet excitation energies. The singlet excitation are compared with two experiments taken from Ref. [Granville 81]. These two experimental data, labeled [exp1] and [exp2] corresponds to absorption experiments at two different temperatures, 293 K and 77 K respectively. We find a very good agreement between calculated and experimental excitation energies, even if care has to be taken in the comparison because our calculations are performed on idealized structures with a fixed alternating bonding independent on the chain length. The whole set of excitation energies for both singlet and triplet states up to 8.3 eV is plotted in the bottom part of Fig.7.6. We see that, at difference of the hydrogen chain, the first bright state lies above dark states. As we will see later this is not the case for the infinite polymer where the first excitation is bright. From our calculations we can observe that the energy difference between the “bright” and “dark” states reduces adding monomers, and in the bigger chain (four monomer) the bright and the dark states have quite the same energies, but the crossover take place for chains longer than the ones we have studied until now.

In conclusion the new first order kernel works very well also for describing the absorption spectra of finite systems, giving an overall agreement with the BS calculations. Minor differences are encountered for the smaller systems we have studied. These differences can be ascribed to the effect of the direct term of the coupling part of the BS equation that is not included in the construction of the kernel.

Next we have calculated in TDDFT the statical axial polarizability for these finite systems both in ALDA and with the new kernel. The axial polarizability is obtained from Eq. (5.29) The results are shown in Fig. 7.7 and 7.8, where the axial polarizability for monomer is plotted in function of the monomer units, and they are compared with previous Hartree Fock and Vignale Kohn calculations present in the literature (see caption). For both systems we find that the $f_{xc}^{(1)}$ kernel, due to its non-locality gives a huge correction to the ALDA, bringing the results close to the more accurate quantum chemistry calculation. Concerning the polyacetylene chain
Figure 7.7: Static axial polarizability per monomer of polyacetylene calculated with TDDFT with the kernel $f_{xc}^{(1)}$ described in section (3.5) at first order (red) compared with the ALDA approximation (black), restricted Hartree Fock (HF) [Kirtman 95] (green) and Current Time Dependent Density Functional Theory with the Vignale Kohn potential (VK) of Ref. [van Faassen 02] (blue).

Figure 7.8: Static axial polarizability per monomer of the $H_{2n}$ chain calculated with the kernel $f_{xc}^{(1)}$ described in section (3.5) at first order (red) compared with the ALDA kernel (black), coupled Hartree Fock (HF) [Champagne 95a] (green) and Current Time Dependent Density Functional Theory with the Vignale Kohn potential (VK) of Ref. [van Faassen 02] (blue). The present results clearly show the beginning of the saturation of the polarizability that is absent in the LDA calculation.
(Fig 7.7) we see that $f^{(1)}_{xc}$ results lies below Hartree Fock and it is very close to the Vignale Kohn calculations of Ref. [van Faassen 02], that for this system turns to be very close to the best available quantum chemical results (see left panel of Fig.7.1). With respect the $H_{2n}$ chain (Fig. 7.8) we have that Vignale Kohn potential gives only a small correction to the ALDA overestimation. The $f^{(1)}_{xc}$ results correct such wrong behavior and approximates the coupled Hartree Fock calculations of Ref. [Champagne 95a], that for the hydrogen chain are known to be similar to the accurate wave functions methods (see right panel of Fig 7.1 and Refs. [Sanchez 03, Kümmel 04, Baer 05, Champagne 95a]).

In summary with the new first order $f^{(1)}_{xc}$ kernel, we describe within TDDFT the excitonic properties of both polyacetylene as a prototype of a $\pi$-conjugated system, and the $H_{2n}$ chain model. Such good description translates in a huge correction of the ALDA axial static polarizability bringing it close to more accurate quantum chemistry methods.

In order to get insight in the mechanism leading to the saturation of the static polarizability with polymer length we plot in Fig. 7.9 and 7.10 the real space exciton distribution $|\Psi_S(r_h, r_e)|^2$ (see Eq. (4.19)) of the electron ($r_e$) coordinate with respect to a fixed hole position ($r_h$) for the bright exciton of the polyacetylene chain and the ($H_{2n}$) chain. For a fixed hole position the excitonic wave function provides insight about the real-space correlation between the hole and electron in the excited state. In Fig. 7.9 in all the chains the hole is placed close to the first carbon atom. We see that for the all chains the excitonic amplitude is concentrated close to the hole and spread all over the entire chains, with maximum values around the single bonds of the chains. In Fig 7.10 for the $H_{2n}$ chain the hole is placed in the middle of the $\sigma$ bond of the first $H_2$ unit. Again, we see that the excitonic amplitude spread along all the chain, and has maximum values in the inter-molecular regions. For the longer chains we can see how the excitonic wave function approaches the infinite limit excitonic length (see Sec. (7.4.2). In this way we can give a new interpretation of the evolution toward saturation of the polarizability with the size of the chain, relating it to the nature of the exciton (localization length). We have that the bulk localization length of the bright exciton is about 12 unit cells in the $H_{2n}$ chain and 20 units in polyacetylene. This translates to the following physical picture: when the size of the chain is larger than the exciton localization length the polymer behaves

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6 For other configurations the VK results are completely wrong, however the present approach works for all $H_{2n}$ configurations
as a bulk system and then the polarizability per unit length saturates to the infinite limit, whereas for smaller sizes the polarizability increases with size. Then all is dictated by the presence of excitons. This picture is clearly justified by our results for the $H_{2n}$ chain and, to a lesser extend by polyacetylene.

Figure 7.9: Excitonic wave functions of the optical active excited states for different trans-polyacetylene chain lengths. In all cases the hole is placed close to the first carbon atom. The wave functions have been normalized to their maximum value.
Figure 7.10: Excitonic wave functions of the optical active excited states for different $H_{2n}$ chain lengths up to $n=7$. In all cases the hole is placed in the middle of the bond of the first $H_2$ units. The wave functions have been normalized to their maximum value.
7.4 Infinite chains

In this section we look at more in detail to the periodic, infinite, chain both for $H_{2n}$ and polyacetylene.

7.4.1 Trans-Polyacetylene

The structure of the polyacetylene polymer has just been sketched in Fig. 7.1, together with the lattice constant in the direction of the polymer axis. The calculated LDA band gap is of 0.78 eV, whereas the GW calculation opens it to 2.13 eV\(^7\). The band structure along the $\Gamma - X$ direction both in LDA and GW approximations is showed in Fig. 7.11, adjusted by placing the Fermi energy at 0 eV. The LDA and GW band structures exhibit similar dispersion, being the main difference the opening of the band gap (scissor operator). We note that as showed in chapter (5) for the $H_{2n}$ chain, the modified cutoff potential speeds up the convergence of the band gap energy with respect to the empty space in the supercell, that is very slow when the bare coulomb potential is used (see top panel of Fig. 7.11). When the cutoff potential is used, we see that a side of 33 a.u. in the directions orthogonal to the chain axis is enough to get a converged band gap value. To obtain a converged GW band structure we have used a one-dimensional grid of 61 $k$ points in the direction of the polymer axis. To calculate the screening we introduce bands up to 35 eV in the electron-hole KS states and a plane wave cutoff of 12 Ry. The converged value of the fundamental direct gap at the X point (2.13 eV), it is very closed to the value reported in Ref. [Rohlfing 99] (2.1 eV) calculated with a localized base code, so without any problem of spurious images interactions. The absorption spectra calculated in the BS framework and in TDDFT with the $f_{xc}^{(1)}$ kernel are plotted in Fig. 7.12. In the same figure we also plot a TDDFT spectrum calculated with the ALDA and the independent quasi particle spectrum, i.e. the spectrum neglecting the electron-hole interaction. Those spectra were calculated considering light with electric field polarization vector parallel to the chain. First we note that in the case of the infinite polymer the coupling term in the excitonic Hamiltonian has no effect in the optical absorption spectrum, so here the resonant approximation for the BS equation is totally justified. Next we see that for this system the agreement of the

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\(^7\) The ground state LDA eigenfunctions and eigenvalues have been obtained using a plane wave energy cutoff of 36 Ry., we have truncated the coulomb potential using the method described in chapter 5, using a supercell of size 4.643x33x33 a.u. and a cutoff radius of 12 a.u.
Figure 7.11: Top: Calculated band gap at X point of trans polyacetylene in GW approximation for different supercell size with bare coulomb and modified coulomb potential described in chapter 5. Calculated band structures of trans polyacetylene along the chain axis in LDA approximation (middle panel) and GW approximation (bottom panel). In both cases, the zero corresponds to the Fermi level.
Chapter 7. Optical absorption of quasi 1D systems

Figure 7.12: Calculated absorption spectrum for the polyacetylene polymer in BS framework and in TDDFT with the $f_{xc}^{(1)}$ kernel, compared with the ALDA calculation and the non interacting quasi-particle spectrum.

TDDFT calculation with the kernel $f_{xc}^{(1)}$ (blue line) is practically indistinguishable from the Bethe Salpeter calculation (black line) and presents a single sharp peak placed at 1.69 eV. Above 2 eV the system is nearly transparent. Such result is in good agreement with the measured spectrum which has maximum absorption at 1.7 eV [Leising 88] and with the previous BS result of Ref. [Rohlfing 99]. Clearly we see that the ALDA spectrum totally fails in the description of the optical absorption of this quasi 1-dimensional system as it does for other insulators (bulk or surfaces). Beyond the bright exciton at 1.69 eV that we now indicate with $S_b$, another bound exciton is found at 1.86 eV with piratically zero oscillator strength that we indicate with $S_d$. Both excitons arise mainly from $\pi \rightarrow \pi^*$ transitions, the spectrum results to be converged including only few bands in the excitonic matrix (we used two valence bands and two conduction bands), and only electron-hole states close to the X point contribute to the formation of the excitons, as just previously observed in Ref. [Rohlfing 99] \(^8\). With respect the triplet excitations, that cannot be excited by

\(^8\) Here we stress that, as previously stated in chapter 5, the one dimensional sampling of the Brillouin zone is allowed thanks to the use of the cutoff coulomb potential, whereas for calculations with the bare coulomb potential a three dimensional sampling is needed in order to get converged results. The plane wave cutoff for the exchange and direct terms of the excitonic
7.4 Infinite chains

Table 7.3: Calculated binding energies in eV of the singlet and triplet excited states of the trans-polyacetylene, compared with the results of previous Bethe Salpeter calculations with different implementations.

<table>
<thead>
<tr>
<th>Trans Polyacetylene</th>
<th>This work</th>
<th>[Rohlfing 99]</th>
<th>[Rohlfing 04]</th>
<th>[Puschnig 03]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singlet</td>
<td>$S_b$</td>
<td>0.44</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>$S_d$</td>
<td>0.27</td>
<td>0.3</td>
<td>0.38</td>
</tr>
<tr>
<td>Triplet</td>
<td>$T_1$</td>
<td>0.91</td>
<td>1.2</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>$T_2$</td>
<td>0.31</td>
<td>0.4</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Figure 7.13: Electron-hole wave functions of the “bright” (1.69 eV) and “dark” (1.93 eV) excitons of the polyacetylene, showing the distribution of the electron relative to the hole fixed at 0 Å. In the top part the excitonic wave function is plotted in the plane where the polymer lie, while in the bottom panel it is averaged in a plane perpendicular to the chain: $\Psi_S(x_e, r_h^0) = \int dr^+_e \Psi_S(x_e, r_h^0)$. With an arrow we have indicated the position of the hole.

Hamiltonian is respectively of 6.8 Ry and 5.8 Ry.
light, we again found two bound excitons, placed at 1.22 eV and 1.82 eV. The binding energies of the singlet and triplet bound excitons found in the present calculation are summarized in Tab. 7.3, together with others Bethe Salpeter calculations. The electron-hole wave functions in real space of the two singlet bound excitons states are depicted in Fig. 7.13. The hole is fixed in an arbitrary position on the polymer chain and is placed in the center of the panels. We see that the first optically active exciton is very extended in space, having a size of about 50 Å, and spreading about 20 unit cells. The second optically inactive excitons is even more extended. The polarizability per monomer unit has been calculated in the same way we did for the finite chains, i.e. in reciprocal space for the new kernel and in configuration space for the ALDA. The polarizability values are 971.2 a.u. in ALDA approximation and 537.19 a.u. with the $f^{(1)}_{xc}$ kernel. Thus, we obtain a huge reduction of the polarizability when the new kernel is used with respect the ALDA value in agreement with the trends found for finite systems.

### 7.4.2 Hydrogen chain

The same study made for the polyacetylene has been performed for the infinite $(H_{2n})$ chain. The structure of the chain has been described in the introduction of this chapter. We have used a supercell of size $4.5 \times 25 \times 25$ a.u., and a cutoff radius of 8 a.u. for the cylindrical cutoff coulomb potential. The ground state wave functions have been obtained with a plane wave energy cutoff of 40 Ry. The quasiparticle band structure along the Γ-X direction in the GW approximation is presented in Fig. 7.14 together with the result. The calculated LDA gap at the X point of the one-dimensional Brillouin zone is 2.28 eV, whereas the GW calculation yield a band gap of 5.49 eV. In order to obtain converged quasiparticle energies we have adopted a one dimensional sampling of the Brillouin zone using 61 k points. The exchange part of the self energy, Eq. (4.16), has been calculated using the same plane wave cutoff used in the computation of the wave functions, while for the correlation part, Eq. (4.17) we have used bands up to 25 eV and a plane wave cutoff of 8 Ry. As in the case of the polyacetylene the LDA and GW band structures are qualitatively similar, and the main change is the gap opening that in the GW is nearly twice the LDA one. Thanks to this we can take in account the GW correction through a scissor operator for the BS calculation and for building $f^{(1)}_{xc}$ in TDDFT. The calculated absorption spectra in different approximation is showed in Fig. 7.15. As in the case of the trans-polyacetylene polymer we observe that the coupling terms can
be neglected in the excitonic Hamiltonian and we can consider only the resonant part. The BS spectrum is showed with a black solid line. When compared with the non-interacting quasiparticle spectra (green line) we observe that the hydrogen chain presents a bound exciton having a large binding energy of 2.03 eV. With respect the TDDFT calculation we see that the $f_{xc}^{(1)}$ reproduces perfectly the BS
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Figure 7.15: Calculated absorption spectrum for the $H_{2n}$ chain neglecting the electron-hole interaction (green), in Bethe Salpeter framework (black), in TDDFT with the ALDA approximation (red) and with the $f_{xc}^{(1)}$ kernel.

As in the case of the polyacetylene the two spectra are practically indistinguishable confirming the fact that also for quasi one-dimensional systems the bound excitons are correctly described in TDDFT when the new first order kernel is used. As expected the ALDA calculation fails to describe the correct optical properties. The effect of the ALDA kernel (red solid line) is to slightly shift

<table>
<thead>
<tr>
<th>Hydrogen molecule chain</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singlet</td>
<td></td>
</tr>
<tr>
<td>$S_b$</td>
<td>2.03</td>
</tr>
<tr>
<td>$S_d1$</td>
<td>0.75</td>
</tr>
<tr>
<td>$S_d2$</td>
<td>0.25</td>
</tr>
<tr>
<td>Triplet</td>
<td></td>
</tr>
<tr>
<td>$T1$</td>
<td>2.81</td>
</tr>
<tr>
<td>$T2$</td>
<td>0.91</td>
</tr>
<tr>
<td>$T3$</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 7.4: Calculated binding energies in eV of the singlet and triplet excited states of the $(H_{2n})$ chain.
7.4 Infinite chains

![Graph](image)

**Figure 7.16:** Excitonic wave functions of the bound excitons of the $H_{2n}$ chain along the chain axis averaged in a plane perpendicular to the polymer. The hole in fixed in the center of the panel and it is placed in the middle of the $H_2$ bond.

The non interacting Kohn-Sham spectra at higher energies. In Fig. 7.15 the non interacting Kohn-Sham absorption spectra it is not depicted for reason of clarity, but it is essentially the non interacting QP spectra (green slide line) shifted by 3.21 eV (the scissor operator) to lower energies. Above the bright excitons placed at 3.46 eV we find other two 'dark' excited states (at 4.74 eV and 5.24 eV) below the quasiparticle gap placed. The binding energies of the bright and darks excitons are summarized in Table. 7.4 together with the corresponding triplet excited states. The triplet excitations binding energies are larger since the repulsive exchange interaction between the electron and hole is absent for spin-triplet excitations. The electron-hole wave functions for the singlet excited states are showed in Fig. 7.16. In the three plots the hole is fixed in 0 and it is in the middle of the $H_2$ bond. We can see that the electron distribution with respect the hole position is more localized than in the case of the polyacetylene, extending over about 40 Å(20 oligomer units). The excitonic wave functions of the higher lying “dark states” are more extended in space. The calculated axial polarizability in TDDFT with the ALDA and the $f_{xc}^{(1)}$ kernel are
respectively 160.9 a.u. and 120.6 a.u.. Berger et al. [Berger 05] found 162.28 a.u. in ALDA approximation and 131.28 a.u. with the Vignale Kohn functional. We see that the non local kernel partially correct the overestimation of the ALDA and gives a better results than the Vignale-Kohn functional even if the calculated value it is still consistently bigger than the Quantum Monte Carlo calculation which is $53.4 \pm 1.1a.u.$.

Role of the ground state wave functions

Until now we have shown how the ALDA fails in the calculation of optical properties of linear chains and how a better description can be achieved either resorting to the Many Body Perturbation Theory via the Bethe-Salpeter equation or using more elaborated non-local kernels that mimics the MBPT results. As described in the introduction, the solution of the BS equation requires as starting ingredient, the ground state wave functions for both occupied and unoccupied states that until now have been calculated within Density Functional Theory in the LDA approximation. In this section we want to quantify the role of the initial wave functions in the calculation of the Bethe-Salpeter absorption spectra. We have repeated the calculation of the absorption spectra in BS framework showed in Fig. 7.15 but instead of using LDA ground state wave-functions we have used exact exchange ground state wave function in the KLI approximation as described in section (1.27). The DFT band gap calculated with these wave functions is 3.0 eV and we have skipped the calculation of the quasi-particle band structure and we adjusted the scissor operator for the KLI calculation in order to have the same quasiparticle band gap of the LDA+GW calculation. In Fig. 7.17 we compare the obtained interacting and non-interacting spectra with the previous calculation made with the LDA wave-functions. The two non-interacting quasiparticle spectra have the same onset by construction. When the electron-hole interaction is considered we see that the use of the KLI wave functions give rise to a bound exciton with a larger binding energy than the LDA+BSE calculation. We have also performed using both LDA and KLI ground state wave-functions a calculation considering the exchange part only in the excitonic Hamiltonian, that is equivalent to the RPA approximation. No differences have been observed between the two calculations, so the observed difference has to be addressed to the direct term, thus the quality of the ground state wave-functions

\textsuperscript{9} Here we do not investigate the impact on the quasi particle energies in the GW approximation, that will require a deeper study and we refer for instance to Ref. [Aulbur 00b].
7.4 Infinite chains

The polarizability per monomer unit computed with the KLI wave-functions turns to be smaller and is 102.2 a.u., but we have to keep in mind that this value has been obtained considering LDA+GW quasiparticle gap. If the use of KLI wave functions opens up the gap more than LDA, then the polarizability will be reduced. This is the subject for future studies.

Role of the bond length

We conclude this chapter considering an hydrogen chain with a very small bond alternating length. The consequence of decreasing the alternating bond length of the $H_{2n}$ chain in the electronic structure is to pass from an insulator or semiconductor to a metallic one dimensional chain in the limit of equal bond length. Here we have considered an infinite one dimensional $H_{2n}$ chain with the same intra-molecular length of the system studied above (2.0 a.u.), but with an inter-molecular distance quite equal to the intra-molecular bonding length (2.05). Such system turns out to have a very small energy gap, and a very different electronic delocalization from the

Figure 7.17: Calculated BS absorption spectra for the $H_{2n}$ chain, using LDA and KLI wave functions. With dashed lines are plotted the quasiparticle spectra neglecting the electron-hole interaction.
Chapter 7. Optical absorption of quasi 1D systems

Figure 7.18: Calculated LDA band structure along the $\Gamma - X$ direction for the infinite $H_{2n}$ chain with an inter-molecular distance $d = 2.05$ a.u..

case studied in the previous section. The unit cell of this linear chain is depicted in the inset of Fig. 7.18 together with the LDA band structure. Comparing with Fig. 7.14 we can see that the band structure is qualitatively similar and the effect of reducing the intermolecular distance between $H_2$ molecules is to reduce the band gap at the $X$ point from $2.28$ eV to $0.26$ eV. Also for this hydrogen chain we have performed a GW calculation that yield a quasiparticle gap of $0.61$ eV. In Fig. 7.19 the absorption spectra in both BS (black) and ALDA (red) are showed together with the corresponding non-interacting quasiparticle spectrum. The BS spectrum shows again a bound exciton with a binding energy of $0.37$ eV. We note that at difference of the systems studied until now, the ALDA furnish a description of the absorption similar to the one calculated solving the Bethe-Salpeter equation. If we look at the electron-hole excitonic wave function of this system, showed in the top panel of Fig. 7.20, we can see that, at difference of the polyacetylene and of the hydrogen chain studied before (bottom panel), it is not spatially localized along the polymer axis. Thus we can see that the bond alternation is responsible for the localization of the excitonic wave function, giving rise to a correlation between the electron and the hole that the local density approximation it is not able to take into account. The more metallic-like nature of the present cases is responsible of the
7.5 Conclusion

In conclusion we have studied with ab initio methods the optical properties of finite and infinite polyacetylene and hydrogen chains, as prototype of in dimensional poly-

Figure 7.19: Calculated absorption spectra of the infinite \( H_{2n} \) chain with an inter-
molecular distance \( d = 2.05 \) a.u. in BS framework (black) and in TDDFT within the
ALDA approximation (red).

Figure 7.20: Excitonic wave functions for the two studied structures of the \( H_{2n} \) chain
with inter-molecular distance \( d = 2.05 \) a.u (top) and \( d = 2.5 \) a.u. bottom.

good performance of LDA for this small band-gap system. The larger the gap the
larger are the excitonic effects and the deviation from the prediction of the LDA.

7.5 Conclusion

In conclusion we have studied with ab initio methods the optical properties of finite
and infinite polyacetylene and hydrogen chains, as prototype of in dimensional poly-
mers. For these class of systems it is known that the TDDFT when used with the local and gradient corrected density functionals, does not give an adequate description. We have performed calculations in many body perturbation theory including electron-hole interactions and in TDDFT using a new non-local and energy dependent kernel. We have showed that this new kernel that until now had been tested on bulk system and surfaces gives very good results also for finite and quasi one dimensional systems when compared to the Bethe Salpeter results. Minor discrepancies encountered for small systems can be associated to the effect of the direct term on the coupling part of the excitonic Hamiltonian (usually neglected for bulk calculations) that it is not taken into account in the construction of the kernel. The great overestimation of the ALDA in the calculation of the polarizability for isolated monomer units is partially corrected when the new kernel is used and we argue that the the polarizability of finite chains approach the infinite limit when the length of the chain reach the characteristic length of the size of the exciton of the infinite chain. Such localization of the electron-hole wave function is due to the bond alternation of the polymer and dictates the saturation of the static polarizability with polymer length.
Photo-electron spectroscopy (PES) is a widely used technique to analyze the electronic structure of complex systems. The advent of high intense ultra-short laser sources have extended the range of applicability of this technique to a vast variety of non-linear phenomena like high harmonic generation, above threshold ionization (ATI), bond softening and vibrational population trapping [Brabec 00, Protopapas 97, Eberly 91]. Furthermore, it has turned femtosecond time-resolved pump-probe PES as a powerful technique for the characterization of the excite-stated dynamics is nanostructures and biological systems [Zewail 94, Schattke 03]. In this chapter we will concentrate on the ATI spectrum [Agostini 79]. It consists in the ionization of atoms, due by the absorption of a number of photons larger than the needed to overcome the ionization threshold. Clearly a high intensity laser is needed and in consequence it is intrinsically a non linear process. The quantity that is measured in the experiment is the energy of the ejected photoelectrons and the spectrum typically presents a number of peaks separated by the photon energy. In general, laser-atom-electron interaction is difficult to treat and approximations are usually done, as treating the fields classically in the dipolar coupling. Those approximations are quite good in the strong-field regime that is relevant for those experiments (short-laser pulses with high peak intensities). In this context it is clear that we need a theory that goes beyond the standard Fermi-Golden rule used to describe theoretically PES: photon-field matrix elements between the occupied initial state and the excited outgoing-wave state. This approach is justified only for low intensity and long laser pulses. For high intensity laser pulses (intensity above $10^{13} W cm^{-2}$) perturbative treatments are no longer suitable because the laser field

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1 This section is largely an adaptation of the article: D. Varsano, M.A.L Marques, H. Appel, E.K.U. Gross and A. Rubio: Photo-electron spectroscopy: a TDDFT approach Unpublished. As such, the reported work includes collaboration of the rest of the authors of the article.

1 For recent theoretical and experimental reviews see the following Refs. [Schattke 03, Petek 00, Almbladh 83, Onida 02] and references therein.
becomes comparable with the Coulomb binding field and non-linear effects arise.
A fully many-body description of PES is prohibited, except for the cases of few (one
or two) electron systems [Grobe 93, Lein 01, Bandrau 03, Faisal 87] and specific
core level excitations [Schattke 03, Almbladh 83]. Therefore, it will be desirable to
have a PES theory based on Density Functional Theory (DFT) where the complex
many body problem is mapped onto a fictitious single electron system. This is the
purpose of the work presented in this chapter: to circumvent the PES many-body
problem by describing photo-electron emission process within a time-dependent-
density-functional (TDDFT) based geometrical-scheme that address directly the
photo-electron current without resorting to linear response. Other works have been
published addressing single and multiple ionization processes within TDDFT, as for
example Refs. [Maitra 01, Pohl 00, Ullrich 00, V.Veniard 03].

Time-dependent density functional theory (TDDFT), as exposed in the previous
chapter, maps the whole many body problem into the time dependence of the density
from which all physical properties can be obtained. The method is in principle ex-
act, however approximations have to be made for the unknown exchange-correlation
functional as well as for the specific density-functional that provides the physical
quantity we are looking for, in particular even if we know how to formally extract
optical absorption and emission spectra from the time-evolution of the dipole mo-
moment as shown in section (2.2.2), we do not know how to express formally the photo-
electron current in terms only of the time-dependent density. Although it would be
desirable to determine the form of the unknown functional of the density describing
the PES, the purpose of this work is to derive a feasible and working scheme to com-
pute the PES of an interacting electron system in terms of the time-dependent single
electron Kohn-Sham orbitals. For independent electrons the derived formula is ex-
act and for interacting electrons we provide formal justification of the equation for
PES based on the propagation of the many-body density matrix. The idea behind
the present work is to follow the TDDFT Kohn-Sham states under the influence of
the external time-dependent laser field. We have implemented this formalism and
performed the calculations solving the TDDFT Kohn-Sham equations in real time
and real-space. The motivation to work with a grid comes from the flexibility in
describing systems that undergo rearrangements and/or bound-to-continuum tran-
sitions and their adaptation to the present fast time-evolution algorithms. Exchange

\[ E = e/(4\pi\varepsilon_0a_0^2) = 5.1 \times 10^9 V/m. \]

\[ I = \varepsilon_0cE^2/2 = 3.51 \times 10^{16} W/cm^2. \]
correlation effects will be described using optimized-effective-potentials (TDOEP). This chapter is organized as follows: in section (8.1) we will describe our approach to calculate the PES in a single-electron picture. In section (8.2) we will give the justification of our approach for a many body problem and finally in section (8.3) we will show the results obtained for a one-dimensional Helium atom model.

8.1 One-electron spectroscopy

Before discussing the main results of the present work, it is important to summarize how the PES can be exactly calculated for a one-electron system once it is perturbed by an external laser-pulse. A lot of work has been done in the past to handle this problem and we refer the reader to references [Brabec 00, Protopapas 97, Faisal 87] for more details.

The most direct and intuitive way to access the PES is to resort to a wave function projection scheme in which all bound-state components of the wave function are projected out; the remaining part gives access to the total electron emission. This approach relies on the fact that during the laser pulse none of the electrons reach the detector, all electron current is measured once the laser is turn-off. By monitoring the time evolution of that projected wave-function we can extract the energy resolved PES by performing a Fourier transform from time to energy. Another equivalent approach starts from the the exact many body wave function $|\psi\rangle$ after the the laser field has been turn-off. The PES will be given just by the following projection of the time-dependent wave-function:

$$P(E) = |\langle \Phi(E) |\psi\rangle|^2 = \langle \psi | \hat{D}(E) |\psi\rangle$$  \hspace{1cm} (8.1)

where $\Phi(E)$ denotes the wave function of an outgoing (unbound) electron of energy $E$ of the laser free Hamiltonian, and $\hat{D}(E)$ is the corresponding projector operator to this continuum of states. Although no time-propagation has to be performed once the laser-field is switched-off, to use this formula we encounter two practical problems: i) we need to know beforehand all the states with positive energy , ii) the final wave-function extends over a large region of space and therefore large simulation boxes will be required to describe it properly, complicating the numerical calculation. These difficulties can nevertheless be overcome for spherical systems using the so-called window operator approximation to $\hat{D}(E)$ [Schafer 91]:

$$\hat{D}(E) = \frac{\Gamma^{2n}}{(\hat{H}_0 - E)^{2n} + \Gamma^{2n}}$$  \hspace{1cm} (8.2)
where $\Gamma$ and $n$ are parameters controlling the broadening of the spectrum, and $\hat{H}_0$ is the ground state Hamiltonian of the system (the resolution of the spectrum is $2\Gamma$). It was found that $n = 2$ provides a good description of the spectrum [Schafer 91]. To extend such a procedure for a many electrons system is not at all trivial even if we can formally define as in Eq. (8.2) a projector operator for a many body system:

$$\hat{D}(E) = \sum_i |\Phi(E)\Psi_i^{N-1}\rangle\langle\Phi(E)\Psi_i^{N-1}|$$

(8.3)

where $|\Phi(E)\Psi_i^{N-1}\rangle$ is the tensorial product between the ket of the bounded (many-body) states of the $N-1$ electron system $\Psi_i^{N-1}$ and the ionized electron with positive energy $E$. Anyway such procedure is very cumbersome and really unpractical to compute for a general many-electron system, as nanostructures or biomolecules.

Inclusion of exchange-correlation effects for a many-electron interacting-system can be achieved within TDDFT where we keep the simplicity of working with a set of time-dependent fictitious single-particle Kohn-Sham orbitals. In spite of having transferred all the many-body problem into an unknown exchange-correlation functional, the lack of a density-functional that provides the electron emission probability is, in principle, a major limitation to directly access the PES from the time-evolution of the density. Therefore, we have to devise a practical scheme that will allow the extraction of PES from the time-evolution of the Kohn-Sham wave-functions.

Within the standard adiabatic approximation to TDDFT there has been few attempts to describe PES and multiple ionization processes [Maitra 01, Pohl 00, Ullrich 00]. All those calculations use the geometrical concept of analyzing box (depicted in the upper part of Fig. 8.1) to separate the bound and continuum parts of the many-body wave functions. Then the emission probability is correlated to the change in the number of bound electrons in time (as done for example in refs. [Maitra 01, Ullrich 00]). An alternative and very simple scheme was proposed in ref. [Pohl 00]. The idea is to record the single-electron (Kohn-Sham) wave-function over time at a point $r_{bc}$ far from the physical system. By Fourier transforming the time-dependent orbitals into the energy domain: $\psi_i(r_{bc}, E)$ the probability of detecting one electron with energy $E$ is given by:

$$P(E) = \sum_i |\psi_i(r_{bc}, E)|^2.$$  

(8.4)

This method is certainly very easy to implement, nevertheless suffers from some drawbacks: the weights of the peaks depends on the measuring point $r_{bc}$, it is
8.1 One-electron spectroscopy

Figure 8.1: Left panel: Schematic description of the geometry used to extract the photo-emission spectrum: region A is our real-simulation box where the electrons where all the interactions occur, whereas region B describes out-going electrons that are considered free-electrons and are not allowed to go back to A. Right panel Standard form of the mask function used in the calculations.

directly based on Kohn-Sham wave functions, without a clear connection to the many body state, it is not gauge-invariant (due to the finiteness of the simulation box), and does not provide angle resolved spectra (unless we take a dense set of measuring points $r_{bc}$ along a sphere enclosing the system under study). In order to overcome some of the those difficulties we resort to a geometrical mask-function approach for the calculation of the photo-electron spectra. We illustrate now the mask-function approach within an effective one-particle formalism (as for TDDFT) and leave the many-body description for next section.

8.1.1 Mask-function approach

This is the approach we follow in the present work. It has some similarities to the schemes discussed above in the sense that we adhere to a geometrical interpretation of the photo-emission process, i.e, we take an analyzing box framework schematically described in Fig. 8.1. Namely, we divide the simulation box into two regions, A and B; the inner region $A$ containing the nuclei and enough space around it and region $B$, defined as the complement of $A$, where the electrons will be considered as independent (outgoing) particles. The transition from A and B is achieved through
a smooth mask function $M(\mathbf{r})$ which is defined to be 1 deep in the interior of A and 0 outside (see Fig. 8.1(right panel)). The advantage of using such approach is that we can store the wave-function in a spatial mesh inside A, while in B the free-electrons can be trivially treated in momentum space. The time evolution is performed in the velocity gauge in order to avoid numerical instabilities at the boundary of the analyzing box. During time evolution part of the density contained in A will go to region B, and from that moment on it will be assumed to be ionized. This is taken into account at each iteration using a smooth mask function $M(\mathbf{r})$ that acts directly to the time-dependent wave-function. The evolution scheme is the following:

$$
\psi^A_i(\mathbf{r}, t + \Delta t) = M(\mathbf{r})e^{-iH\Delta t}\psi^A_i(\mathbf{r}, t)
$$

$$
\psi^B_i(\mathbf{p}, t + \Delta t) = e^{-i(p - A(t))^2/2\Delta t}\psi^B_i(\mathbf{p}, t) + \tilde{\psi}^A_i(\mathbf{p}, t + \Delta t) \quad (8.5)
$$

where $H$ is the single-particle Hamiltonian, $A(t)$ is the vector potential associated to the electric field of the laser pulse, and $\tilde{\psi}^A_i(\mathbf{p}, t + \Delta t)$ is the Fourier transform of the part of the wave function $\psi^A_i$ that have left the region A in the time step $\Delta t$ i.e:

$$
\tilde{\psi}^A_i(\mathbf{p}, t + \Delta t) = \int d\mathbf{r}(1 - M(\mathbf{r}))e^{-iH\Delta t}\psi^A_i(\mathbf{r}, t)e^{i\mathbf{p} \cdot \mathbf{r}} \quad (8.6)
$$

The evolution is performed until no appreciable density leaves region A. In this scheme there is no constrain about when the electron is emitted, either during or after the laser pulse has been applied, however the simulation box A has to be large enough in order to minimize the error stemming from neglecting the possibility that electrons in region B come back into region A. This size would clearly depend on the laser parameters: intensity, frequency and pulse shape.

As the electrons in region B of the simulation box are considered free it is tempting to identify these as photo-electrons, and then write momentum-resolved photo-electron spectra as:

$$
P(\mathbf{p}) = \sum_i |\psi^B_i(\mathbf{p}, t \rightarrow \infty)|^2 \quad (8.7)
$$

the total kinetic-energy PES is obtained integrating over angles Eq. (8.7):

$$
P(E_p = p^2/2) = \int d\Omega_p \sum_i |\psi^B_i(\mathbf{p}, t \rightarrow \infty)|^2, \quad (8.8)
$$

similarly, the angle-resolved spectra comes straightforwardly through a partial integration with respect to the absolute momentum transfer $p$:

$$
P(\theta_p, \phi_p) = \int dp \sum_i |\psi^B_i(\mathbf{p}, t \rightarrow \infty)|^2, \quad (8.9)$$
where the momentum angular coordinates $\theta_p, \phi_p$ are held fixed in a given reference frame. For non-interacting electrons, the calculation of PES using Eqs.(8.7-8.9) is formally correct as the only real approximation is neglecting the recoiling of electrons that reach region $B$ while the laser is on, however this can be easily control by changing the size of $A$. However, in this case also the much simpler approach or Ref. [Pohl 00] described in Eq. (8.4) will provide an exact description of the total photo-electron current. On the other hand, for an interacting many-body system it would be desirable to provide some formal justification of Eq. (8.7) besides the heuristic approach described here. This is done in the following section where we establish a link between the photo-electron current and the time evolution of the interacting many-body density-matrix.

### 8.2 Many-body photo-electron spectroscopy

As for one-electron system, the knowledge of the time evolution of the many-body wave function contain the relevant information to compute the PES. The most direct approach would be to project out all bound-state components and the remaining is the desired integrated photo-electron spectra. Of course, this scheme is not practical for many-electron systems as we need not only the full-time-dependent wave function but also the complete knowledge of the whole bound-state spectra (see Eqs.8.3). Still, it is illustrative to show how we could get around the problem of the bound states by using once more the geometrical approach of Fig. 8.1 discussed in the previous section. Let us illustrate the scheme for the case of two-electron system perturbed by a short-laser-pulse. The mask function should be applied only to one of the two spatial coordinates for the wave-function, as integrating over the other coordinate will provide the emission probability, or more precisely, the probability of having one electron in region $B$. In practice, we evolve in time the wave-function in region $A$ with the full two-electron Hamiltonian $H$, mask the second coordinate and Fourier transform to momentum space the part of the wave-function ($\tilde{\psi}^A$) leaving region $A$:

\begin{align}
\tilde{\psi}^A(r_1, r_2, t + \Delta t) &= (1 - M(r_2))e^{-iH\Delta t}\psi^A(r_1, r_2, t) \\
\tilde{\psi}^A(r_1, p, t + \Delta t) &= \int dr_2 \tilde{\psi}^A(r_1, r_2, t + \Delta t)e^{i p \cdot r_2} \\
\psi^B(r_1, p, t + \Delta t) &= e^{-iH_1 + i(p_2 - A(t))^2}\Delta t}\psi^B(r_1, p, t) \\
&+ \tilde{\psi}^A(r_1, p, t + \Delta t) \\
&= (1 - M(r_2))e^{-iH\Delta t}\psi^A(r_1, r_2, t) \\
&+ \int dr_2 \tilde{\psi}^A(r_1, r_2, t + \Delta t)e^{i p \cdot r_2} \\
&+ e^{-iH_1 + i(p_2 - A(t))^2}\Delta t}\psi^B(r_1, p, t) \\
&+ \tilde{\psi}^A(r_1, p, t + \Delta t) \\
&= (1 - M(r_2))e^{-iH\Delta t}\psi^A(r_1, r_2, t) \\
&+ \int dr_2 \tilde{\psi}^A(r_1, r_2, t + \Delta t)e^{i p \cdot r_2} \\
&+ e^{-iH_1 + i(p_2 - A(t))^2}\Delta t}\psi^B(r_1, p, t) \\
&+ \tilde{\psi}^A(r_1, p, t + \Delta t)
\end{align}
where now the Hamiltonian that controls the time-evolution does not have the electron-electron repulsion term and the propagation of coordinate 2 is assumed to be the one corresponding to a free-particle whereas coordinate 1 evolves with the remaining $H_1$ part of the full-Hamiltonian $H = H_1 + H_2 + V(1,2)$. Now the photo-electron spectra reads:

$$P(p) = \lim_{t \to \infty} \int d_{r_1} |\psi^B(r_1, p, t)|^2.$$  

Therefore we only need to accumulate in time the wave-function in region $B$. Of course Eq. (8.11) reduces to Eq. (8.7) in the case of independent electrons. Still this approach for general interacting electron systems is computationally unpractical and one would like to use Eq. (8.7) for PES calculations. In the next two sections we will try to provide a formal justification for this approach by looking at the time-evolution of the Wigner transform of the one-body density matrix and by performing a simple population analysis, i.e. looking how many electrons leave the arbitrary simulation box.

### 8.2.1 Density-matrix approach

The one-body density matrix of the system of $N$ particles is defined as:

$$n(r, r') = \int d(r_2...r_N)\Psi(r, r_2, ..., r_N)\Psi^*(r', r_2, ..., r_N),$$  

where $\Psi$ denotes the full many-body wave-function. This expression is simplified if one works with independent particles; in this case $\Psi$ is a Slater determinant and Eq. (8.12) reduces to: $n(r, r') = \sum_{i}^{occ} \psi_i(r)\psi^*_i(r')$, with $\psi$ the one-body orbitals that in the case of DFT, they correspond to the Kohn-Sham eigenfunctions. It is important to note that the Kohn-Sham density matrix is not equal to the full many-body density matrix even if their diagonals (i.e. the density) are equal. This can be seen from the fact that the Kohn-Sham is idempotent whereas the exact one is not. The probability of finding a $N$-electron system in one of its possible (positive) charge states, related to electron emission, can be formally written [Ullrich 00], but simplifications are due to have a formulation in terms of KS single particle orbitals. In order to make connection with a classical description of photo-electron emission, it is convenient to extend the classical concept of phase-space distribution to the quantum regime. A common approximation for a quantum phase-space distribution function comes from the the Wigner transform of the density matrix with respect
8.2 Many-body photo-electron spectroscopy

the center of mass coordinate \( \mathbf{R} = (\mathbf{r} + \mathbf{r'})/2 \). This Wigner transformation is defined as [Baym 62]

\[
 w(\mathbf{R}, \mathbf{p}) = \int d\mathbf{s} e^{i \mathbf{p} \cdot \mathbf{s}} n(\mathbf{R} + \mathbf{s}/2, \mathbf{R} - \mathbf{s}/2), \tag{8.13}
\]

where \( \mathbf{s} = \mathbf{r} - \mathbf{r'} \) is the relative position. This function it is normalized and its integral over the whole space (momentum) give the probability density to finding an electron with momentum \( \mathbf{p} \) (position \( \mathbf{R} \)):

\[
 \int \frac{d^3 \mathbf{p}}{(2\pi)^3} w(\mathbf{R}, \mathbf{p}) = \int \frac{d^3 \mathbf{p}}{(2\pi)^3} \int d^3 s e^{i \mathbf{p} \cdot \mathbf{s}} n(\mathbf{R} + \mathbf{s}/2, \mathbf{R} - \mathbf{s}/2) = n(\mathbf{R}, \mathbf{R}) = n(\mathbf{R}) \tag{8.14}
\]

\[
 \int d^3 R w(\mathbf{R}, \mathbf{p}) = \int d^3 R \int d^3 s e^{i \mathbf{p} \cdot \mathbf{s}} n(\mathbf{R} + \mathbf{s}/2, \mathbf{R} - \mathbf{s}/2) = \int d^3 (r_2...r_N) |\Psi(\mathbf{p}, r_2...r_N)|^2 = n(\mathbf{p}). \tag{8.15}
\]

Note that uncertainty principle prevents the knowledge of \( \mathbf{r} \) and \( \mathbf{p} \) simultaneously, therefore \( w(\mathbf{R}, \mathbf{p}) \) cannot be a proper joint distribution function. Assuming now that the Wigner function in Eq. (8.13) is a good approximation for the joint-distribution function, we can use the geometrical procedure discussed in previous section and monitor in region B of Fig. 8.1 the time-evolution of the joint-distribution function for the system of interest. In this case we can resort to the classical definition of photo-electron spectra (PES) based on the knowledge of the phase-space distribution function:

\[
P(E = p^2/2) = \int_B d\mathbf{R} w(\mathbf{R}, \mathbf{p}) \tag{8.16}
\]

In this Eq. (8.16) the function \( w(\mathbf{R}, \mathbf{p}) \) should be evaluated a long time after the laser has been turn off in order to have all the ionized density contained in region B.

At this point we should make contact with an effective single-particle theory as TDDFT and derive the equivalent equation of Eq. (8.16) for Kohn-Sham orbitals. It is clear from our previous discussion that the stationary one-body Kohn-Sham density matrix is given by

\[
n_{KS}(\mathbf{r}, \mathbf{r'}) = \sum_{i=1}^{\text{occ.}} \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r'}) \tag{8.17}
\]
The density matrix (8.17) can be written in the following way:

\[
n_{KS}(\mathbf{r}, \mathbf{r}') = \sum_i \left[ \psi_i^A(\mathbf{r})\psi_i^{A*}(\mathbf{r}') + \psi_i^A(\mathbf{r})\psi_i^{B*}(\mathbf{r}') \\
+ \psi_i^B(\mathbf{r})\psi_i^{A*}(\mathbf{r}') + \psi_i^B(\mathbf{r})\psi_i^{B*}(\mathbf{r}') \right] \tag{8.18}
\]

We can see that first term, containing the product of the wave function in region \(A\), does not contribute to the integral of Eq. (8.16). We expect that the contribution of the next two terms that correspond to overlaps of a localized wave function with an unlocalized is negligible, so Eq. (8.16) reads:

\[
P(E) \simeq \int_B d\mathbf{R} \int d\mathbf{s} e^{i\mathbf{p}\cdot\mathbf{s}} \sum_i \psi_i^B(\mathbf{R} + \mathbf{s}/2)\psi_i^{B*}(\mathbf{R} - \mathbf{s}/2) \tag{8.19}
\]

As the probability of finding an ionized electron in the region \(A\) is small we can extend the integration over \(B\) to the whole space and after some algebra we obtain:

\[
P(E) \simeq \sum_i |\psi_i^B(\mathbf{p})|^2. \tag{8.20}
\]

We have found the same Eq. (8.7) as the wave-functions appearing in Eq. (8.20) correspond to the evaluation of the Wigner function long after the pulse has been switch off \((t \to \infty)\).

### 8.2.2 Population analysis

We have already derived Eq. (8.20) following two different paths. Here we add another one by looking at the time evolution of the number of electron leaving a region delimited by a surface \(S\) (where the molecule is situated):

\[
N_S(t_1) = 1 - \int_{\Omega_S} d\mathbf{r} n(\mathbf{r}, t_1) = - \int_{t_0}^{t_1} dt \int_{\Omega_S} d\mathbf{r} \dot{n}(\mathbf{r}, t), \tag{8.21}
\]

where with \(\Omega_S\) we have indicated the volume contained in the surface \(S\), and \(t_0\) is a time before the laser is switched on and the total charge density of the system is still inside the surface \(S\). Using the continuity equation the number of electrons leaving \(S\) is given by:

\[
N_S(t_1) = - \int_{t_0}^{t_1} dt \int_{\Omega_S} d\mathbf{r} \nabla \cdot \mathbf{j}(\mathbf{r}, t) \tag{8.22}
\]
Using the relation that connect the current $j$ to the Wigner function defined in Eq. (8.13):

$$j(r, t) = \int \frac{dp}{(2\pi)^3} p w(r, p, t)$$

we can express the $N_S$ as

$$N_S(r_1) = \int \frac{dp}{(2\pi)^3} \left[ \int dt \int d\mathbf{r} \cdot p w(r, p, t) \right]$$

$$\equiv \int \frac{dp}{(2\pi)^3} P(p).$$

We can analyse the quantity inside the square bracket in Eq. (8.24) as the desired photo-electron spectrum. This can be make more clear by using Gauss theorem to convert the volume integral in Eq. (8.24) into a surface integral; thus the photo-electron spectrum reads

$$P(p) = \int_{t_0}^{t_1} dt \int_S dA \mathbf{p} w(r, p, t).$$

So, we are measuring the current passing through a surface $S$ far away from the system, that is a very intuitive image of an ionization process. Until now all derivation has been general, now in order to get a manageable expression we approximate the Wigner function by its Kohn-Sham counterpart (as in the previous section). After inserting the Fourier transforms of the Kohn-Sham wave functions we get:

$$w(r, p, t) = \sum_i \int \frac{dk}{(2\pi)^3} e^{-2i(k-p) \cdot r} \psi_i^B(k, t) \psi_i^{B*}(2p - k, t).$$

Using the fact that after the laser is switched-off the electrons outside $S$ (region B in Fig. 8.1) propagate in time as free particles:

$$\psi_i^B(k, t) = e^{-i \frac{k^2}{2}(t-t_0)} \psi_i^B(k, t_0)$$

gathering Eqs.(8.24),(8.26),(8.27) we obtain:

$$P(p) = \sum_i \int_{t_0}^{t_1} dt \int d\mathbf{r} \int \frac{dk}{(2\pi)^3} \left[-2i(k-p)\right] \mathbf{p} e^{-i \frac{k^2}{2} (2p - k)^2} \times$$

$$\times e^{-2i(k-p) \cdot r} \psi_i^B(k) \psi_i^{B*}(2p - k).$$
where we have put \( t_0 = 0 \) for sake of simplicity. Now we can perform analytically the integration over time in the limit \( t_1 \to \infty \) and then take the limit of the radius of the sphere \( R_S \to \infty \). Taking into account the result:

\[
\int_0^\infty dt e^{-i t} = \frac{i}{\epsilon}
\]  

we obtain:

\[
P_p = \sum_i \int d\mathbf{r} \int \frac{d\mathbf{k}}{(2\pi)^3} 2(\mathbf{k} - \mathbf{p})] \cdot \mathbf{p} \frac{e^{-2i(\mathbf{k} - \mathbf{p}) \cdot \mathbf{r}}}{\frac{k^2}{2} - \frac{(2p-k)^2}{2}} \psi_i^B(\mathbf{k}) \psi_i^{B*}(2\mathbf{p} - \mathbf{k})
\]  

\[ (8.30) \]

If we now perform the \( \lim R_S \to \infty \), and integrate \( \mathbf{r} \) over all space, we get:

\[
P_p = \sum_i \int \frac{d\mathbf{k}}{(2\pi)^3} 2(\mathbf{k} - \mathbf{p})] \cdot \mathbf{p} \frac{\delta(\mathbf{k} - \mathbf{p})}{\frac{k^2}{2} - \frac{(2p-k)^2}{2}} \psi_i^B(\mathbf{k}) \psi_i^{B*}(2\mathbf{p} - \mathbf{k})
\]

\[
= \sum_i |\psi_i^B(\mathbf{p})|^2.
\]

\[ (8.31) \]

and Eq. (8.7) is once more obtained.

---

\(^3\) we note here that if we first take the limit \( R_S \to \infty \), and perform the space integral, we will get zero as one would expect.
8.3 Results

To illustrate how the many-body based procedures work we look a simple one-dimension two-electrons atom model. It is described by a nucleus of positive charge fixed at the origin at \( z = 0 \) and two electron whose spatial coordinates are indicated by \( z_1 \) and \( z_2 \). Its bare Hamiltonian is:

\[
H_0 = \frac{1}{2}p_1^2 + \frac{1}{2}p_2^2 + V(z_1) + V(z_2) + V(z_1 - z_2) \tag{8.32}
\]

Both the attractive electron-ion and the repulsive electron-electron interaction is modeled by the so-called soft Coulomb potential\[Grobe 93\].

\[
V(z) = -\frac{1}{\sqrt{z^2 + 1}} \tag{8.33}
\]

The potential (8.33) is a realistic model for ionization studies: it has the correct coulombic asymptotic behavior and is a way to allowing in 1D for the possibility that the electrons pass by the nucleus and by each other without probing a Coulomb singularity. The total potential \( V(z_1, z_2) \) (electron-ions and electron-electron interaction) is plotted in Fig. 8.2. We see that the potential is symmetric with respect the \( z_1 = z_2 \) and \( z_1 = -z_2 \) diagonals and the "hill" along \( z_1 = z_2 \) indicates that it is not energetically favorable to find both electrons on the same side of the nucleus. Now we apply a laser pulse, the time-dependent velocity-gauge Schrödinger equation, in atomic units, for the two electron wave function \( \Psi(z_1, z_2, t) \) is:

\[
i\frac{\partial \Psi}{\partial t}(z_1, z_2, t) = \left[ \sum_{i=1}^{2} \left( \frac{p_i - A(t)}{2} \right)^2 - \frac{2}{\sqrt{z_i^2 + 1}} + \frac{1}{\sqrt{(z_1 - z_2)^2 + 1}} \right] \Psi(z_1, z_2, t) \tag{8.34}
\]

where \( z_i \) are the electrons coordinates, \( p_i \) are the canonical electron momenta and \( A(t) = -\int_0^t \varepsilon(t')dt' \) is the vector potential associated to the electric field of the laser pulse \( \varepsilon(t) = \varepsilon_0 f(t, T_{\text{pulse}})\sin(\omega t) \) with amplitude \( \varepsilon_0 \) and frequency \( \omega \). With \( f(t, T_{\text{pulse}}) \) we have indicated an envelope function.

For the Kohn-Sham solution of the problem we use an exact exchange functional \( v_x(z, t) \), namely a time-dependent optimized-effective-potential Eq. (1.26) that for two-electrons is half of the Hartree potential:

\[
v_H(z, t) = \int \frac{n(z', t)}{\sqrt{(z - z')^2 + 1}} dz' \tag{8.35}
\]

\[
v_x(z, t) = -\frac{1}{2}v_H(z, t) \tag{8.36}
\]
Chapter 8. Photo-electron spectroscopy in TDDFT framework

Figure 8.2: The total potential $V(z_1, z_2)$ as a function of the two one-dimensional electron coordinates $z_1$ and $z_2$.

i.e. the Kohn-Sham Hamiltonian is

$$H_{KS} = \frac{(p - A(t))^2}{2} - \frac{2}{\sqrt{z^2 + 1}} + v_H(z, t) + v_z(z, t). \quad (8.37)$$

For this simple case we can perform the time evolution of this one-dimensional soft-core He atom exact Eq(8.34), and within the TDOEP approximation Eq(8.37). The time-evolution of the wave function has been performed following the split-operator method [Feit 82]: the unitary evolution operator $U(t - t_0) = \exp[-iH(t - t_0)]$, for a small increment time-step can be decomposed in three steps as:

$$U(\Delta t) = e^{-i(T+V)\Delta t} = e^{-iT\frac{\Delta t}{2}}e^{-iV\Delta t}e^{-iT\frac{\Delta t}{2}} + O(\Delta^3) \quad (8.38)$$

The action of the kinetic energy operator is easily performed in Fourier space $^4$. The ground state wave function $\Phi_g(z_1, z_2)$ is computed evolving always according to Eq. (8.38) the Schrödinger equation (8.34) replacing the time-step $\Delta t$ by an imaginary time-step $-i\Delta \tau$. In this way any arbitrary initial seed function relaxes to the ground state wave function after a sufficient amount of imaginary time.

$^4$ If we write the action of the electromagnetic field in velocity gauge as in Eqs (8.34 and 8.37), the term $\exp[-i\frac{(p - A(t))^2}{2}]$ is treated in Fourier space.
Figure 8.3: Snapshots of the probability density for He soft core. The two axis represents the coordinates of the two electrons. Exact (left panel) and TDOEP (right panel). Upper panel: ground state. Middle panel, the laser pulse in turned on (after 5 optical cycle). Bottom panel: End of the pulse (40 optical cycles).
First we look at the probability density $|\Psi(z_1, z_2)|^2$ as a function of time before, during, and just at the end of a short laser pulse. In this calculation we used a laser pulse with a linear ramp as envelope function: $f(t) = t/t_{\text{ramp}}$ for $t \leq t_{\text{ramp}}$ and $f(t) = 1$ for $t > t_{\text{ramp}}$, $t_{\text{ramp}}$ is the time needed to ramp the pulse. The laser has a wavelength $\lambda = 400 nm$ and intensity $I = 10^{14} W/cm^2$. The duration of the laser pulse is of 40 optical cycles and 2 cycle are used to ramp the pulse. The results are plotted in Fig. 8.3. From these snapshot we can see that electron-correlation effects are already relevant at the ground-state level (upper panel): the Kohn-Sham density probability is more extended and has less structure than the exact one. This gets more dramatic as the laser is turn on, the Kohn-Sham particles move faster and are uncorrelated, in contrast the exact density probability exhibit off-diagonal components that are clear manifestation of the role of electron-correlations absent in the TDOEP description. The question now is to analyze what is the impact of this correlations in the total PES. To further illustrate this discussion about the impact of approximating the interacting density-matrix by the Kohn-Sham density matrix, we have taking the previous case and instead of using the TDOEP, we have build the exact Kohn-Sham potential, and initial Kohn Sham wave functions associated
Figure 8.5: Difference in absolute value between the one-body density matrix of the many body system and the Kohn-Sham system Eq. (8.17) at initial time (on the left) and after the interaction of the system (on the right) with a laser pulse of 20 cycles at intensity $I = 10^{15} \text{W/cm}^2$ and $\omega = 1.47 \text{a.u.}$ ($\lambda = 31 \text{nm}$). in a square of 16 a.u. around the origin Fig. 8.4.

To the initial many-body density: $\psi_{ks} = \sqrt{n_{gs}/2}$. In this case we have used a laser pulse of 20 cycles with a wavelength $\lambda = 31 \text{nm}$ and intensity $I = 10^{15} \text{W/cm}^2$. The envelope function is of the form: $f(t) = \sin^2(\pi t/T_{\text{pulse}})$. The laser pulse is showed in Fig. 8.4. Then we propagate the Kohn-Sham system with a TDOEP only exchange potential. In Fig. 8.5 we show the difference in absolute value between the one-body density matrix of the many body system and the Kohn-Sham system (Eq. (8.17)) before and after the interaction with the laser field. We can see that at initial time (left part of the figure) the diagonal (i.e. the density) turn out to be the same by construction of the Kohn-Sham system, while after the laser interaction differs due to the lack of a correlation term in the Kohn-Sham Hamiltonian. If one does the same analysis done with the density-matrix in section 8.2.1 but now for a two-electron process, namely two-electron spectroscopy, we would end up in

$$P(p_1, p_2) = \sum_i |\psi_i^B(p_1)|^2 \sum_j |\psi_j^B(p_2)|^2 - \sum_{ij} \psi_i^B(p_1) \psi_j^B(p_2) \psi_j^{B*}(p_2) \psi_i^{B*}(p_1)$$

for the case of only two electrons it reduces to

$$P(p_1, p_2) = |\psi^B(p_1)|^2 |\psi^B(p_2)|^2$$

which is just the product of the probability of emitting one particle. Therefore no correlation in the two-electron process is accounted for. This deficiency should be traced back to the fact that we approximated the interacting density matrix by its Kohn-Sham form.

Now we can address how relevant the differences are when the PES is calculated.
Chapter 8. Photo-electron spectroscopy in TDDFT framework

Figure 8.6: Photo-electron spectrum calculated via Eq. (8.16) for the two electron 1D soft coulomb Many-body system and Kohn-Sham system after excitation with a laser pulse of 2.07fs, $I = 10^{15} W/cm^2$ and $\omega = 1.47 a.u. (\lambda = 31 nm)$ Fig. 8.4. With $s$ are indicated the number of photons absorbed.

via Eq. (8.16) for the exact many-body solution or for the corresponding Kohn-Sham system. This is shown in Fig. 8.6. The used laser pulse is the same described above and showed in Fig. 8.4. A good agreement between the Many-body and Kohn-Sham PES is obtained both for peaks position and intensities. For this small system the correlation seems not to play an important role. The position of the ATI peaks can be estimated by

$$E_s = s\hbar\omega - I_p - U_p$$  \hspace{1cm} (8.39)

where $s$ is the number of photons absorbed, $I_p$ is the single electron ionization potential and $U_p = E^2/4\omega^2$ is the ponderomotive energy that we evaluate at the maximum of the field $E_0$. These estimations are indicated by vertical bars. In order to get stable results for these calculation we used a simulation box that extends over 500 a.u. with a spacing of 0.4 a.u. and a time-step of $2.068 \times 10^{-4} \text{fs}$. Such big boxes are needed to ensure that all the ionized density is contained in the region $B$, so this method can be applied only to small one-dimensional systems for numerical
8.3 Results

Figure 8.7: Photo-electron spectrum calculated via Eq. (8.16) and via Eq. (8.20) after excitation with the same laser pulse of Fig. 8.6. For the latter we have used a simulation box i.e region A of 500 a.u., the laser pulse is the same of Fig. 8.4. In green the spectrum calculated with the method of Ref.[Pohl 00], Eq. (8.4) is shown.

In Fig. 8.7 we plot the energy spectra obtained with the mask function method described in Sec. 8.1.1 Eq. (8.20) and via the direct calculation of the integral Eq. (8.16) for the 1D model considered above. The good agreement between the two curves confirm that the approximations made to obtain Eq. (8.20) are justified even if the mask function produces a background noise. The mask function used here to join the region A and B see Fig. 8.1 is of the form:

\[ M(z) = \sin^2\left(\frac{(L_A+L_m-z)\pi}{2L_m}\right) \]

where \( L_A \) is the size of the region A and \( L_m \) is the length considered from the transition to pass from region A to B (here 10 atomic units). We have checked the stability of the method with respect the \( L_m \) length and the mask shape. Only minor effect has been observed if \( L_A \) is sufficiently large. In the same figure is also plotted the energy spectra following the method of Ref.([Pohl 00]), (Eq.8.4), with \( r_{bc} \) choose near the edge of the simulation box. In this particular one dimensional case we observe a good agreement with the mask method if the measuring point is taken far.
off enough the interaction zone.

In conclusion we have presented a non-perturbative approach for the calculation of the photo-electron spectra that allows to extract integrated above-threshold-ionization spectra of molecular structures. Within the geometrical concept of the mask-operator convergent ATI spectra is obtained. Femtosecond time resolved pump-probe experiments can be modeled within the present scheme with a very low computational cost compared with full many-body-based schemes as we will show in the next chapter. Of course, the lack of good exchange-correlation functionals for strong-non-linear phenomena is a major drawback. This is clearly seen when trying to describe the non-sequential double ionization yield of He and Ne, where the experimental results are several orders of magnitude larger than TDDFT calculations using standard functionals [Petersilka 99, Lappas 98, Bauer 01].
9 Two photon-photoemission spectra of Cu metal surfaces

9.1 Introduction

In this chapter we apply the methodology described in the previous chapter for the calculation of photo-electron-spectroscopy to study Two-Photon Photo-emission (TPPE) [Giesen 85, Haight 95, Fauster 95] spectra and Time-Resolved Two-Photon Photo-emission (TR-TPPE) [Schoenlein 88, Schoenlein 90]. In TPPE, intense laser radiation is used to populate an unoccupied state with the first photon (pump) and subsequently such electron in the intermediate state is ejected by the second photon (probe). In TR-TPPE, the probe pulse which ionize the intermediated state is delayed with respect the pump pulse which populates it, thus providing a direct measurement of the intermediate state lifetime. Here we want to study the TPPE and TR-TPPE for two metal surfaces: Cu(100) and Cu(111). The presence of a metal surface creates electron states that do not exist in the bulk metal. These states can be classified into two groups, according to their charge density localization with respect the surface atomic layer: crystal-induced and image-potential induced surface states. The former are localized mainly at the surface atomic layer [Tamm 32, Shockley 39], while the latter lie mainly in the vacuum region of a metal surfaces with a band gap near the vacuum level. The symmetry breaking on the surface is responsible for the so-called crystal-induced surface states, whereas image states are caused by the long-range tail of the image potential induced at the surface. An electron situated at a distance $z$ from the metal surface experiments an attractive force, $F(z) = -e^2/(2z)^2$, equivalent to that produced by its image charge situated at distance $z$ inside the metal. For large $z$, the potential generated by this surface induced charge approaches the classical image potential, $V(z) = -e^2/4z$.

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† This section is largely an adaptation of the article: D. Varsano, M.A.L Marques and A. Rubio: Time and energy-resolved two photon-photoemission of the Cu(100) and Cu(111) metal surfaces. Computational Material Science 30, 110 (2004). As such, the reported work includes collaboration of the rest of the authors of the article.
Figure 9.1: Schematic picture of a TPPE experiment for a typical metallic surface with a surface band gap close to the Fermi level. The energy $\hbar \omega_a$ (red) corresponds to the pump photon and $\hbar \omega_b$ (green) to the probe photon in TPPE. On the right side we show the tail of the image potential, the densities of the surface state and first three image potential states of Cu(100) (blue) calculated with the model potential of Ref.[Chulkov 99b], and their corresponding binding energies. By $E_F$, $E_{lower}$ and $E_{vac}$ we denote respectively the Fermi energy, the lower edge of the energy gap and the vacuum energy.

This expression corresponds to assuming an infinite repulsive barrier at the surface. In the more general case we have

$$V(z) = -\frac{e^2}{4(z - z_{im})} \frac{\epsilon - 1}{\epsilon + 1}$$  \hspace{1cm} (9.1)

where $z_{im}$ is the position of the image plane (that depends on the electronic and structural properties of the surface), and $\epsilon$ is the static dielectric constant of the surface. When the metal has a surface band gap near the vacuum level, the electrons below the vacuum level are trapped between the well of the image potential and the surface barrier. These quantized states correspond to image potential states, and are spatially localized in the region in front of the surface (see Fig. 9.1). Metal image states typically have a large spatial extension, but barely penetrate the bulk metal. They form a Rydberg-like series with energies, $E_p$, approximately given
9.1 Introduction

by [Echenique 78, Echenique 90, Echenique 02]:

\[ E_p = -\frac{0.85}{(p+a)^2} \text{[eV]}, \quad p = 1, 2... \]  

(9.2)

where \( p \) is a positive integer, and \( 0 \leq a \leq 0.5 \) represents the quantum defect (which depends on the position and width of the gap). The energy of an electron trapped in an image state and moving parallel to the surface with momentum \( k_\parallel \) is therefore:

\[ E = \frac{\hbar^2 k^2}{2m_e} + E_n \]  

(9.3)

In contrast to bulk states, the small overlap between surface states and bulk states reduces considerably the inelastic electron scattering, leading to a long lifetime, \( \tau_p \), of the image states, that scales asymptotically with the quantum number \( p \) as [Echenique 78, Echenique 90]

\[ \tau_p \propto p^3 \]  

(9.4)

Furthermore, image states play an important role in the laser induced chemical control of reactivity at metal surfaces. It is therefore not surprising the considerable number of studies focusing on this subject. \(^1\) Due to this fact, these states are very interesting for the study of electron correlations and their long lifetime make the ideally suited as intermediated state in TPPE. Recently, and with the advent of ultrafast laser technology it became possible to perform time-resolved TPPE spectroscopy (TR-TPPE), which allowed the direct measurement of the lifetime of image states, and with the technique of quantum beat spectroscopy [Höfer 97, Klamroth 01], this measurement is allowed even for states with large quantum number \( p \). The TPPE technique for metal surfaces is depicted schematically in Fig. 9.1. One photon (pump), of energy \( \hbar \omega_a \), excites an electron from an occupied state below the Fermi energy \( (E_F) \) to an image-potential state of quantum number \( p \); Then a second photon (probe), with energy \( \hbar \omega_b \), ejects the electron out of the surface, above the vacuum energy. This electron has a kinetic energy \( E_k = \hbar \omega_b - E_p \), that is measured in a detector far away from the surface. By varying the delay between the pump and probe pulses, the intensity of the TPPE signal as a function of the delay will reflect the evolution of the population of the state \( p \). From this information it is then possible to extract the lifetime of the state \( p \). Surface and image potential states of different surfaces have been observed experimentally [Fauster 95, Schuppler 92, Schoenlein 88, Schoenlein 90, McNeil 97, Shumay 98]. and lifetimes

\(^1\) see Ref. [Echenique 00] and references therein.
of image states for different metal surfaces have been calculated in the framework of the self-energy formalism in the GW approximation [de Andres 87, de Andres 89, Osma 99b, Sarria 99, Chulkov 98, Chulkov 97, Echenique 00]. The results obtained happen to be in rather good agreement with experiments. For example, the calculated [Echenique 00] lifetime of the first three image potential states of the Cu(100) surface are $\tau_{1}^{\text{theor}} = 30\text{fs}$, $\tau_{2}^{\text{theor}} = 132\text{fs}$, and $\tau_{3}^{\text{theor}} = 367\text{fs}$, while the experimental values [Höfer 97] are $\tau_{1}^{\text{exp}} = 40 \pm 6\text{fs}$, $\tau_{2}^{\text{exp}} = 110 \pm 10\text{fs}$, and $\tau_{3}^{\text{exp}} = 300 \pm 15\text{fs}$, while for the first image state of Cu(111) surface the theoretical lifetime is $\tau_{1}^{\text{theor}} = 17.5\text{fs}$ and the experimental [McNeil 97] is $\tau_{1}^{\text{exp}} = 15 \pm 5\text{fs}$.

In the following sections we will describe the calculations made on energy-resolved TPPE spectra of Cu(100) and Cu(111) surfaces. The theoretical approach is based on the propagation of an electron wave-packet as described in the previous chapter and the mask function method is used to calculate the photo-emission spectra. We have used a one-dimensional model potential [Chulkov 99b] simulating the Copper surfaces. The finite electronic lifetimes of the image potential states are taken into account by an empirical self-energy term. The details of calculation will be described in the next section. In this approach the potential is fixed during the whole simulations, i.e., the change of the electronic screening during the excitation is not taken into account. This change could be important for short laser excitations as done in TR-TPPE. In order to assert the relevance of this approximation we will show performed time-dependent simulations of the Copper surface, but including the change of the Hartree potential due to the electronic excitations.

### 9.2 Description of the model for Cu(100) and Cu(111) surfaces

To model the Copper surface we used a one-dimensional slab of 48 Copper layers, surrounded by 290 a.u. of vacuum on each side. The large portion of vacuum is necessary in order to describe the four first image potential wave functions (see Fig. 9.1). The bulk and image potentials are modeled by the one-dimensional potential model of Ref. [Chulkov 99b]. This model potential reproduces the key properties of image states and the position and energy width of the gap, and also the binding energies of the Shockley surface state and the $p = 1$ image state are chosen as fitting
parameters. This potential has the following form:

\[
V(z) = \begin{cases} 
A_{10} + A_1 \cos \frac{2\pi z}{a_s}, & z < \frac{D}{2}, \\
A_{20} + A_2 \cos [\beta (z - \frac{D}{2})], & \frac{D}{2} < z < z_1, \\
A_3 \exp[-\alpha (z - z_1)], & z_1 < z < z_{im}, \\
-\frac{1}{4(z-z_{im})}[1 - e^{-\lambda (z-z_{im})}], & z_{im} < z,
\end{cases}
\]

(9.5)

where the \( z \) axis is taken to be perpendicular to the surface, \( D \) is the width of the system, \( a_s \) is the interlayer spacing and \( z_{im} \) is the position of the image plane. The origin is placed at \( z = 0 \). This model potential has 10 parameters, \( A_{10}, A_1, A_{20}, A_2, A_3, \alpha, \beta, z_1, \lambda \) and \( z_{im} \), but only four of them are independent. \( A_{10}, A_1, A_2 \) and \( \beta \) are chosen as adjustable parameters, and the other six parameters are obtained from the continuity conditions of the potential and its first derivative everywhere in space. \( A_1 \) and \( A_{10} \) reproduce the width and position of the energy gap, respectively. \( A_2 \) and \( \beta \) are chosen to reproduce experimental or first-principles binding energies of the \( p = 0 \) or Shockley surface state and the \( p = 1 \) image state at the \( \Gamma \) point. In this model the number of bulk states is discrete for each value of \( q \parallel \), and is related to the number of layers in the simulation. We do not believe that this is a major limitation, essentially because all the relevant physics occurs close to \( E_F \), while the remaining states mainly act as a polarizable background. The electrons are allowed to move and interact only in the \( z \)-direction, perpendicular to the surface, and we assume a parabolic dispersion in the parallel direction. Within this approximation, the Hamiltonian describing such system can be written as:

\[
\hat{H}_0 = -\frac{d^2}{dz^2} + \hat{v}_\text{model}.
\]

(9.6)

This operator is discretized in real-space using a grid-spacing of 0.2 a.u, which is sufficiently small to allow for a proper description of the relevant electronic states. The model potential together with the calculated first eigenstates of (9.6) is plotted in Fig. 9.2 for the Cu(100) and Cu(111) surfaces. At \( t = 0 \) we assume the system to be in the ground-state of the Hamiltonian (9.6). We then propagate this state with the new Hamiltonian:

\[
\hat{H}(t) = \hat{H}_0 + \hat{v}_\text{laser}(z,t) + \hat{\Sigma}(z),
\]

(9.7)

where \( \hat{v}_\text{laser}(z,t) \) describes a laser polarized in the \( z \) direction that reads, in the length gauge, \( \hat{v}_\text{laser}(z,t) = zE(t) \). The electric field is composed of a pump and a
Figure 9.2: Model potentials for the Cu(111) and Cu(100) surfaces. In red the first surface states are plotted. Figure adapted from Ref.[Osma 99a].
9.2 Description of the model for Cu(100) and Cu(111) surfaces

Figure 9.3: Electric field of the laser pulse used in the study of the Cu(100) surface in function of time: $h\omega_{\text{pump}} = 4.7 \text{ eV}, h\omega_{\text{probe}} = 1.8 \text{ eV}, \sigma_{\text{pump}} = 95 \text{ fs},$ and $\sigma_{\text{probe}} = 54 \text{ fs},$ the delay between the beginning of the pump and probe pulse is $t_D = 120 \text{ fs}$

The electric field of the laser pulse is plotted in Fig. 9.3. The third term $\hat{\Sigma}(z)$ in Eq. (9.7) is added in the Hamiltonian in order to take into account the finite lifetime of the image potential states. It is a time-independent self-energy operator of the form:

$$\Sigma(z) = -i \sum_{k=1}^{N} \Gamma_k |p_k \rangle \langle p_k|$$

where $|p_i \rangle$ are the image potential states and $\Gamma_k$ are the inverse experimental lifetimes of each state taken from Ref. [Echenique 00]. Note here that $\hat{H}(0) = \hat{H}_0$. The time-propagation is performed in real-time following the method described in the previous chapter.
9.3 Energy-resolved spectra

The energy-resolved photo-electron spectra is obtained following the mask method
technique described in the previous chapter. As explained before we divide the
simulation box in two regions. The region, A, containing the slab and the region
where the first image potential states lie, and another, B, defined as the complement
of A. In region B the electrons are considered free outgoing particles, and are treated
in momentum space. The separation between the two regions is achieved through
a smooth masking function, $M$, defined as one in the interior of region A and zero
outside (see Fig. 9.4). The method, described in section (8.1.1) consists in evolving
the wave-packet in the region A with the Hamiltonian (9.7), and mask the orbitals at
each time-step. The electrons that “leave” region A are then treated as free-particles
and accumulated in momentum space. Looking at Eq. (8.20) the Energy-resolved
photo-electron spectrum is identified as:

$$P(\sqrt{2mE}) = \sum_{k=1}^{N} |\psi^B_k(p, t \to \infty)|^2$$  \hspace{1cm} (9.11)

where $N$ is the total number of electrons. In Fig. 9.5 we depict the energy resolved
spectra of a Cu(100) and a Cu(111) surfaces for both zero and finite pump-probe
delay. For the (100) surface, the binding energies of the first image potential states
9.3 Energy-resolved spectra

Figure 9.5: Photo-electron energy resolved spectra of a Cu(100) (left panel) and a Cu(111) (right panel) surfaces for both zero and finite pump-probe delay.

are -0.57, -0.18, and -0.08 eV (see Fig. 9.1), while for the (111) surface the first states are at -0.82, -0.22 and -0.009 eV. Note that the second and third image states of the Cu(111) surface are resonances. Furthermore, the laser parameters used in these calculations were, for the (100) surface, $\hbar \omega_{\text{pump}} = 4.7 \text{ eV}$, $\hbar \omega_{\text{probe}} = 1.8 \text{ eV}$, $\sigma_{\text{pump}} = 95 \text{ fs}$, and $\sigma_{\text{probe}} = 54 \text{ fs}$, and for the (111) surface, $\hbar \omega_{\text{pump}} = 5.1 \text{ eV}$, $\hbar \omega_{\text{probe}} = 1.8 \text{ eV}$, $\sigma_{\text{pump}} = 87 \text{ fs}$, and $\sigma_{\text{probe}} = 50 \text{ fs}$. From these results we observe that the peaks corresponding to the first image potential state are obtained at the correct energy position. The signal due to the image states of higher quantum number cannot be distinguished due to the small difference in energy that cannot be resolved with our grid resolution. We also note that, for zero delay, the broadening of the peak relative to the first image potential state is larger in the case of the Cu(100) surface than in the Cu(111). This is due to the fact that in the former case, the probe pulse can 'pump' low lying energy electrons from the bulk into energy levels near the gap which can be then ejected from the surface by the pump pulse. As the Cu(111) surface has a different electronic structure, such situation does not occur. Note that Cu(100) shows an intrinsic surface state resonance, while Cu(111) has a surface state
below the Fermi level. In the last case, the dominant transition happens between the occupied surface state and the first image potential state. This can be rationalized in terms of the larger spacial overlap between surface and image states as compared to bulk states.

### 9.4 Time-resolved spectra

The typical energy width of the laser pulses used in TR-2PPE varies between about 10 and 30 meV. With this energy resolution it is possible to excite separately each one of the first three image potential states of Cu(100). By following the TR-2PPE intensity in function of the pump-probe delay it is then possible to follow the evolution of the population of these states. In Fig. 9.6 we present calculations of the populations of the first three image states of Cu(100). The curves were obtained by propagating the system with the Hamiltonian (9.7) and projecting out the time dependent wave-function onto the considered image potential states:

$$ Pop_i(t) = |\langle \psi_i^{imag} | \Phi(t) \rangle |^2 $$  \hspace{1cm} (9.12)

For comparison we also show the experimental data from Ref. [Höfer 97]. Clearly, there is a good qualitative agreement between the theoretical and experimental...
9.4 Time-resolved spectra

Figure 9.7: Population of the first image potential state of Cu(100) calculated with and without the term of Eq. (9.14) for a 29 fs laser pulse of energy $\hbar \omega = 4.2$ eV. In both cases the maximum value of the population has been normalized to one. The difference in the lifetime for the two cases is 2%

curves. In these calculations, the electron-electron interaction was taken into account by the model potential of Ref. [Chulkov 99b] described in section (9.2). However, the variation of this term with time was mostly neglected. Part of the time-dependence is taken indirectly into account through the self-energy operator, but one can question how reasonable this approximation really is. In order to answer to this concern, we performed simulations in which we allowed the classical part of the electron-electron interaction (i.e. the Hartree term) to change with time. This was achieved by adding to the Hamiltonian (9.7) a new term, $\delta v_{\text{Hartree}}(z,t)$, that corresponds to the variation of the Hartree potential due to the change of electronic density in the direction perpendicular to the surface,

$$\frac{\partial^2 \delta v_{\text{Hartree}}(z,t)}{\partial z^2} = -4\pi \delta n(z,t).$$

(9.13)

where $\delta n(z,t) = n(z,t) - n(z,0)$. The potential $\delta v_{\text{Hartree}}(z,t)$ can be calculated at each time-step, solving the equation [Liebsch 87]:

$$\delta v_{\text{Hartree}}(z,t) = \int dz' e^{-k|z-z'|} \left[ \frac{2\pi}{k} \delta n(z',t) + \frac{k}{2} \delta v_{\text{Hartree}}(z',t) \right]$$

(9.14)
Note that Eq. (9.14) implies Eq. (9.13) regardless of the values of $k$. Exchange and correlation effects were treated as before, i.e. through the self-energy term (9.10) used to simulate the lifetime of the states. The evolution of the population of the first image state with and without this term is shown in Fig. 9.7. We observe only a minor shift of the peak to lower times from 24fs to 21.3fs and the lifetime is reduced by around 2% when the term of Eq. (9.13) is included. This result validates previous studies that have neglected this effect [Osma 99b, Sarria 99, Chulkov 98, Chulkov 99a].

In conclusion we have performed dynamical simulations in order to calculate energy-resolved photo-emission spectra of the Cu(100) and Cu(111) metal surfaces. We see that the methodology described in chapter (8) gives reliable results for PES. Using the same technique we also obtained time-resolved photo-emission spectra for individual excitations of the first three image potential states of Cu(100). This technique is quite general, and can be used to gain insight on the dynamics of image states with large quantum number and when more than one eigenstate is excited coherently (the situation in quantum beat spectroscopy). Furthermore, we have studied the influence of the variation of the Hartree potential during the excitation. This effects turn out to be small (around 2%).
A Publications

During the PhD period


In Preparation

- D. Varsano, A. Marini and A. Rubio *Excitonic properties of quasi-1d systems: from finite chains to infinite polymers*
• D. Varsano, A. Marini and A. Rubio *Optical spectra and EELS of atomic chains*.


• M. Gruening, A. Marini, D. Varsano, L. Wirtz, P. Garcia Gonzalez and A. Rubio *Combining MBPT and TDDFT for static and dynamic properties of nanosstructures and solids*

• D. Varsano, R. Di Felice, M.A.L. Marques and A. Rubio *Circular dichroism within TDDFT of DNA bases and base pairs*

**Previous publications**


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Bibliography


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